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LIST OF ABREVIATIONS

AOP	Advanced Oxidative Processes
BET	Bruner, Emmett, Teller
CCC	Critical Coagulation Concentration
CEC	Cation Exchange Capacity
COD	Chemical Oxygen Demand
ESI–TOF	Electrospray Ionization-Time-Of Flight
GAC	Granular Activated Carbon
LC-MS	Liquid Chromatography–Mass Spectrometry
LDH	Layered Double Hydroxides
MCL	Maximum Contaminant Level
MCM	Mobil Composition of Matter or Mobil Crystalline Materials
MRM	Multiple Reactions Monitoring
Mt	Montmorillonite
MWCNTs	Multiwalled Carbon Nano Tubes
OA	Oxalic Acid
OCMC	Oxalate-Cation- Montmorillonite Complex
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
POPs	Persistent Organic Pollutants
SBA	Santa Barbara Amorphous type materials
SEM	Scanning Electron Microscopy
SMX	Sulfamethoxazole
TOC	Total Organic Carbon
VOC	Volatile Organic Compounds
XRD	X-Ray Diffraction

LIST OF SYMBOLS AND UNITS

A	Ampere
°C	Degree Celsius
g	Gram
k	Reaction Rate Constant
L	Liter
M	Mole per Liter
m^2	Meter Square
n	Reaction Order
S	Second
V	Volt
λ	Wavelength

RÉSUMÉ

Parmi les différentes voies de traitement de l'eau, l'ozonation est la plus prometteuse lorsque une minéralisation totale des polluants organiques est ciblée. Ceci est surtout le cas de traitements des eaux riches en polluants dans les dérivés d'oxydation partielle sont toxiques pour la santé humaine et la biodiversité. L'ozone est un oxydant puissant, mais sa faible solubilité dans l'eau est un inconvénient majeur. Il existe un intérêt croissant vers des méthodes d'ozonation hétérogènes et catalyseurs qui améliorent la rétention de l'ozone dans le milieu aqueux. À cet égard, les matériaux microporeux, tels que les aluminosilicates et les minéraux argileux présentent de bonnes performances dans les procédés d'ozonation catalytique. Parmi les différents échantillons de montmorillonite, Co(II)Mt et Fe(II)Mt se sont avérés être les plus performants dans la minéralisation d'acide oxalique aqueux. Le pH initial de la concentration du mélange réactionnel, le temps de traitement à l'ozone et la concentration en catalyseur ont montré une forte influence. L'utilisation d'une dose élevée d'ozone (90 mg $O_3.L^{-1}$) a permis d'élaborer un 3^k plan factoriel avec 27 essais d'ozonation pour chaque catalyseur dans des temps raisonnables pour une évaluation rapide des effets individuels et de l'interaction du pH initial et de la concentration de catalyseurs sur la décomposition de dérivés aussi réfractaires que l'acide oxalique. Une minéralisation totale de celui-ci a été obtenue après seulement 15 minutes à pH 2.87 avec 1.88 $g.L^{-1}$ de Co(II)Mt, et le pH 2.88 avec 1.91 $g.L^{-1}$ de Fe(II)Mt. Ces conditions opératoires optimales ont été prises comme référence pour une étude comparative de la réactivité envers l'ozone de divers polluants conventionnels tels le chlorobenzène, l'acide benzoïque, 4-nitrobenzoïque, le 3-hydroxybenzaldéhyde, le 4-nitrophénol, et le phénol. Ceux-ci ont été utilisés comme molécules sondes qui possèdent des structures similaires à celles des intermédiaires d'oxydation du sulfaméthoxazole. La technique HPLC-spectrométrie de masse a révélé que le temps de dégradation est inversement proportionnel à la taille moléculaire. La décomposition de l'acide oxalique est l'étape la plus difficile (déterminante) vers une minéralisation totale, étant un "goulot d'étranglement" dans l'oxydation de toute molécule organique. Ainsi, une minéralisation totale de l'acide oxalique est un gage d'efficacité pour une dégradation avancée de polluants organiques plus complexes. Hormis, le bioxyde de carbone, une telle minéralisation produit également des NOx et des SOx, qui peuvent être éliminés par des traitements ultérieurs appropriés.

MOTS-CLÉS: Catalyse hétérogène; Catalyseurs à base d'argile; Ozonation catalytique; Polluants organiques; Procédés d'oxydation avancée.

ABSTRACT

Among the various water treatment paths, ozonation is most promising when total mineralization of organic pollutants is targeted, more particularly for treating waters rich in pollutants whose oxidation derivatives are harmful for human health and biodiversity. Ozone is a powerful oxidizing agent, but its low solubility in water is a major drawback. There is a growing interest towards heterogeneous ozonation methods and catalysts that enhance ozone retention in the aqueous medium. In this regard, microporous materials such as aluminosilicates and clay minerals exhibit high effectiveness in catalytic ozonation processes. Among the different samples of montmorillonite, Co(II)Mt and Fe(II)Mt turned out to be the most efficient in the mineralization aqueous oxalic acid. The initial pH of the concentration of the reaction mixture, the ozone treatment times and the amount of the catalyst showed strong influence. The use of a high dose of ozone (90 mg $O_3.L^{-1}$) allowed to achieve a 3^k factorial design with 27 ozonation tests for each catalyst in reasonable times for a quick evaluation of the individual effects and the interaction of the initial pH and concentration of the catalysts derived from decomposition as refractory as oxalic acid. Total mineralization of the latter was obtained after only 15 minutes at pH 2.87 with 1.88 gl-1 Co(II)Mt, with pH 2.88 and 1.91 g.L-1 Fe(II)Mt. These optimal operating conditions were taken as a reference for a comparative study of the reactivity of ozone toward various conventional pollutants such as chlorobenzene, benzoic acid, 4-nitrobenzoic acid, 3-hydroxybenzaldehyde, 4-nitrophenol and phenol. The latter were used as probe molecules which have similar structures to those of the oxidation intermediates of sulfamethoxazole. The HPLC-MS technique revealed that the degradation time is inversely proportional to the molecular size. The oxalic acid decomposition is the most difficult stage, i.e. a kinetic-controling step towards total mineralization, being a 'bottleneck' in the oxidation of any organic molecule. Thus, total mineralization of oxalic acid is an efficiency guarantee for advanced degradation of complex organic pollutants. Except, carbon dioxide, such mineralization also produces NOx and SOx which can be eliminated by appropriate further treatments.

KEYWORDS: Heterogeneous catalysis; Clay catalysts; Catalytic ozonation; Organic Pollutants; Advanced Oxidation Processes

CHAPTER I

INTRODUCTION

Pollutant organic chemicals in drinking water consist of several compounds of natural and industrial origin (Daud *et al.*, 2010; Kjellström *et al.*, 2006; Nidheesh and Gandhimathi, 2012; Elsousy *et al.*, 2007; Giordano *et al.*, 2007; Mantzavinos, 2003). Unfortunately, man-made industrial chemicals are increasing in number and in concentration in water supplies as a result of effluent discharge, spills and intentional dumping (Munter, 2006; Beltran *et al.*, 2005; Negrel *et al.*, 2012). The concern about the toxicity of organic compounds in drinking water was justified. These pollutant organic molecules in drinking water can be categorized in several ways (Wang and Fiessel, 2008; Can and Gurol, 2003; Cooper and Burch, 1999). Common procedures for classifying the organic chemicals were based on their volatility, polarity, and their carcinogenic potential. The latter was a specific classification of a more general topic of organic compounds impact on human's health (Scholtz and Van Heyst, 2012). The organic compounds studied in the present thesis were among the common chemicals whose application in industrial plants was necessary as intermediate compounds for production of other added value chemicals. Besides the type and the nature of these molecules, the employed decontamination technique is also a matter of importance. There are numerous methods for their elimination. The problem with biological techniques is controlling and monitoring the remediation conditions under which the bacteria or fungi should continue their normal life (Diez, 2010; Ito *et al.*, 1996; Ren *et al.*, 2007; Azzouz, 2012). Physical processes are acceptable for sizeable contaminants especially in processes such as filtration. In other physical methods such as coagulation and flocculation, toxic sludges are sometimes produced. Even aeration is not effective enough, since in this process only

volatile compounds are subject to elimination. Besides, in physical processes toxic properties of pollutants remain untackled (Ramirez *et al.*, 2010; Wang and Fiessel, 2008; Koohestanian *et al.*, 2008; Mohan, 2014; Rahni and Legube, 1996; Kwong *et al.*, 2008; Kasprzyk-Hordern *et al.*, 2003; Henry and Beaudry, 1984; Stuber *et al.*, 2005). In this situation, chemical methods of decontamination may attract the attention. In fact, the use of chemicals in the treatment of drinking and (or) waste water is unavoidable. Unfortunately, in many practical cases the evaluation of the applied chemicals for this purpose was directed primarily at performance and cost, not on whether components of the chemicals or by-products of the process might present a toxicological hazard to the consumer. This is the reason why oxidation methods are preferable to saponification and chlorination techniques. The latter produces undesirable by-products. When chlorination techniques are employed, chlorinated organic compounds are formed which are among dangerous and toxic chemical compounds. Besides, many previous works have clearly demonstrated that incomplete oxidative treatment may produce sometimes even more hazardous waters than untreated waters (Scholtz and Van Heyst, 2012; Diez, 2010; Numata *et al.*, 2005). Waste-waters emerging from industrial zones unfortunately enter to the natural water streams by one way or another. Therefore, they should be treated in a manner that not only the parent pollutants are degraded but also these toxic by-products resulting from some treatment processes do not exceed the critical level (Khankhasaeva *et al.*, 2004). Unavoidable contamination of potable water sources with industrial process waters obliges to lower the organic contamination content of waste-waters and ideally to totally mineralize them. Among the existing chemical techniques, some attract the intention more than others mainly because of safety measures. There are essentially some major concerns that have to be addressed to evaluate the safety of a chemical compound that is used for remediation of water supplies. The most important factor for choosing a chemical compound for treatment processes is the safety to humans consuming the water. Carcinogenic and

toxicological properties of such remediation chemicals are matter of concern. Application of ozone in ozonation processes fulfills the above mentioned conditions. Moreover, given its short life time, ozone decomposes readily and quickly in water without inducing negative health effects. In water, ozone decomposes almost spontaneously into oxygen after 2-3 min at ambient temperature and pressures. There exists an ample literature in this regard. (Scholtz and Van Heyst, 2012; Kumar and Sathyamurthy, 2013; Rice *et al.*, 1982, p. 255–285). Catalytic ozonation is expected to produce higher performances in the ozonation of organic pollutants, because of, at least, the additional contribution reagents to solve partly the issue of ozone solubility and short lifetime. All these aspects required an ample documentation before proceeding to test our catalysts in the oxidative decomposition of the investigated organic molecules. For this purpose, the present thesis was structured in five parts, namely:

1. Chapter 1: An introductive section that exposes the context, objectives and the approach tackled to attain these objectives. The originality of the present thesis resides in an innovative concept that total mineralization of any hazardous and refractory organic pollutants is possible only via synergistic parameter interactions. The present thesis aims to demonstrate that effective ozonation can be achieved in the presence of optimum amount of adequately modified clay-based catalysts in moderately acidic media, and that such operating conditions can be adapted to each organic substrate to be decomposed. For this purpose, the approach adopted consisted in structuring the research and the present thesis in five parts: an introduction section that explains the context of the issue of total mineralization of organic pollutants, objectives and steps for attaining these objectives, followed by three published works taken as three consecutive chapters, along with a final conclusion that gather the main findings of this research.

2. Chapter 2, exposes the main issue to be addressed in this thesis, namely the oxidative decomposition of organic pollutants in waters. This chapter consists of the first article, which is structured in two part; 1. a first one which provides a deep analysis of the achievements made so far in this regard, confers to ozonation a privilegied role in future water treatments to be designed, and makes emphasis on the relatively high performance of heterogeneous catalysts in the ozonation of a wide variety of organic pollutants; 2. a deep analysis of the main findings provided by literature, which allow concluding that effective ozonation requires the presence of 1. a solid surface that can favor adsorption for compensating the shortcomings related to the low solubility and short lifetime of ozone in aqueous media; 2. electric charges on the solid surface, which can exert interaction with ozone in all its forms (bubbles, dissolved and adsorbed) and dispersed organic molecules and 3. the simultaneous presence of both Lewis acidity and conjugated basicity through the mere presence of exchangeable cations (Lewis acidity) and surrounding lattice oxygen atoms (Lewis basicity). These features appear as essential requirements for achieving both reagents adsorption and surface reaction, which already impose as catalyst aluminosilicates such as clay minerals and zeolites and other mixed oxides counterparts. Such solid catalysts may also promote the formation of active complex on the surface (Azzouz *et al.*, 2010; Azzouz, 2012; Canton *et al.*, 2003; Guo *et al.*, 2012; Legube and Karpel Vel Leitner, 1999). Such a surface active complex involves the bridging of bivalent cations between negative surface charges belonging to two parallel clay sheets (Fig. 1.1). Nevertheless, each cations is expected to display specific physicochemical properties, as a results of its electropositivity and solvation grade. Eletropositivity increases in the following sequence Cu < Ni< Co<Fe, and appears to play a key role in the surface interaction first with the exchangeable site and with the adsorbed and non-adsorbed species in the vicinity of the catalyst surface.

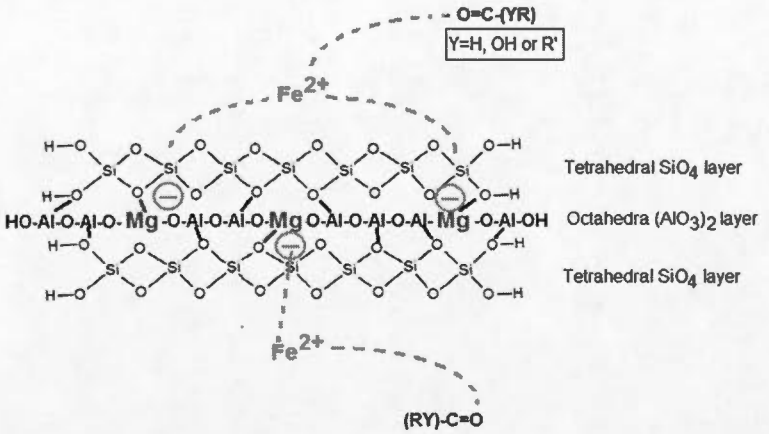


Fig. 1.1 Cation bridging effect between the negatively charged clay surface and organic species with high electron density (oxalate anion, carboxylate anion, alcohol, aldehyde, undissociated carboxylic acids).

Another significant finding resides in the simultaneous occurrence of ozonation processes in both the solid porosity and bulk solution, since ozone appears to react in all its adsorbed and dispersed forms, and that there is no essential need to hydroxyl radicals in acidic media, as long as the chemical stability of the solid surface is preserved. The very structure of the aluminosilicate was found to play a key role through the extent of the solid surface and porosity, inasmuch as unlike zeolites and pseudo-zeolitic counterparts, lamellar and swellable structures such as clay minerals do not display pore diffusion constraints. Clay based catalysts may be suitable for achieving ozonation of a wide scope of organic substrates. The state-of-the-art in the catalytic ozonation of organic pollutants may be useful to understand the contribution of the solid surface. The latter is expected to involve interactions between adsorbed and (or) unadsorbed species including mobile cations in the vicinity of the catalyst surface. Equilibrium conversion required different ozonation times according the exchangeable cation. Under similar operating conditions, different electropositivities impose different cation retention strength on the clay surface and different Brönsted acidities according to the number of solvating water molecules around each cation. These two factors, among many others, produce different cation mobility and loss in

time by slight and reversible ion-exchange and leaching in the vicinity of the clay surface. One may emphasize that, for the same pH, larger clay amounts enhance clay-clay interactions and coagulation-flocculation. This phenomenon is strongly influenced by the nature of the exchangeable cation. Unlike bivalent cations, which display bridging effect on the clay compaction, monovalent cation such as Na+ causes clay dispersion because of similar positive charges on both sides of each clay lamella as long as clay-clay interactions and, thereby, detrimental coagulation-flocculation do not play a significant role. Clay-clay interaction may be more or less influenced by the nature of the exchangeable cation and pH changes.

Since in this chapter other oxidative methods such as Fenton was discussed, it should be clarified that unlike Fe^{2+} cations, which act as precursor of $^{\bullet}OH$ radicals in the presence of hydrogen peroxide, more particularly at elevated pH, Fe^{3+} behaves as quencher for H_2O_2, inducing its decomposition into oxygen and water without generating hydroxyl radicals. The latter displays a higher oxidation potential (Reaction 1.1).

$$^{\bullet}OH + H^{+} + e^{-} \rightarrow H_2O \qquad E^{0} = 2.33\ V \qquad (1.1)$$

This is higher than that of ozone which is 2.07 volts at pH 0 and a $pO_3/\ pO_2$ ratio of 1. pH showed a significant role in abatement of organic compounds; higher pH values were detrimental for all catalysts, but beyond neutral pH, ozonation was found to weakly reactivate again mainly because of the enhancement in the formation of hydroxyl radicals, which promotes the predominance of radical pathway.

3. Chapter 3 also consists of a published paper, which uses all these findings and others as starting hypotheses for investigating the ozonation process. This was achieved taking oxalic acid, one of the most refractory compounds towards ozone, as

a reference probe molecule. In our ozonation attempts an average value of usual oxalic acid concentrations in most polluted waters and wastewaters were utilized. Higher concentrations cannot be justified, while lower concentrations are limited by the accuracy of COD measurements. Based on the ample literature reviewed in the first part of chapter 2, the issue of total mineralization of organic compound has been tackled using a judicious approach. The latter aims to demonstrate that total mineralization of oxalic acid into carbon dioxide can be achieved in the presence of optimum concentration of a clay mineral adequately modified at optimum acidity that enables cation mobility and slight ion-exchange without affecting the catalyst structure. Investigations in this regard revealed a strong interaction between these two parameters, whose synergy appears to be much more beneficial for oxalic acid mineralization than their separate individual effects. In other words, this paper provides clear evidence that there exists an optimum pH for a given amount of a given type of catalyst. Here, one may explain that mathematically, any convexity, concavity or inflection point is an optimum point that requires that the first derivate function is equal to zero. In scientific language, optimum also means ''best compromise'', since 79.5% Na^+ replaced by Fe^{2+} gave similar COD removal as 100%, 79.5% is the best compromise possible affording high COD removal with less iron. Lower catalyst amounts are not sufficient for adsorption, while higher values enhance lamella-lamella interaction and partial coagulation-flocculation of the clay mineral. This finding is of great importance, because it allows envisaging that optimum conditions for total mineralization of refractory compounds such as oxalic acid may also be suitable for total degradation of heavier organic substrates. Such an approach is based on a hypothesis according to which the reactivity towards ozone increases with increasing molecular weight but decreasing oxidation state of the organic substrate. This approach was verified in Chapter 4, where different catalysts were tested for ozonation attempts. In all catalytic ozonation processes Fe(II)Mt showed almost similar performances as Co(II)Mt, but slightly higher. This catalyst

was selected for deeper investigations due to many reasons, such as: 1. Co(II) cations is more toxic and more expensive than Fe(II); 2. This allows comparison with most oxidation and AOP processes in water, which have been tested in the presence of Fe(II) cations as catalysts. There exists an ample literature in this regard. 3. The lower oxidation potential of $Co^{2+}(aq) \rightarrow Co^{3+}(aq)$ of -1.81 eV as compared to that $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$, which is of -0.77 eV. Such oxidation potentials make that $Fe^{2+}(aq)$ can be more readily oxidized in the presence of ozone in $Fe^{3+}(aq)$ as compared to $Co^{2+}(aq)$. $Co^{3+}(aq)$ precipitation triggers around pH 3, and slight pH increase during ozonation may cause catalyst loss. As a detail for catalyst preparation it is worth mentioning that Fe(II) content in fully ion-exchanged montmorillonite was assessed as the value of the cation exchange capacity (CEC) provided by ion-exchange isotherm measurements. XR-fluorescence gave also similar Fe(II) content in fully ion-exchanged samples. CEC was also used for estimating the M(II) cation contents with a relative error not exceeding 2%. The iron content of the catalyst samples was 100% (fully exchanged) unless otherwise stated.

For the purpose of clarity it is worth mentioning that Fig. 3.4 shows the evolution in time as determined by periodical measurements, on the other hand Fig. 3.11 shows a theoretical curve based on mathematical model, whose adequacy and accuracy is maximum around the (0,0,0) points. Such models belongs to the centered-rotative category, and are usually employed for assessing optimum parameter values around a suspected center of cube (or hypercube) that includes the variation ranges of the parameters considered. Such models should not be used at the edges of the cube because of accuracy loss. Both figures are in agreement showing an optimum ozonation time around 15 min. Besides, Quadratic terms express the convexity of the response-surface describing the effect of a given parameter (appendix M). High values of these coefficients indicate accentuated convexity, which allows accurate assessment of the optimum parameter value. Conversely, low values of the quadratic

terms gave flattened response-surfaces with difficult localization of the optimum. Coefficient a_{33} has the highest values, which accounts for the most pronounced convexity of the response-surface describing the effect of pH. The negative sign of this quadratic term corresponds to a maximum in this response-surface.

4. Chapter 4 aims to demonstrate this hypothesis, by applying the optimal conditions for total mineralization of oxalic acid to a fairly wide scope of organic molecules, most of them being recognized as being harmful pollutants for both human health and biodiversity. The latter are supposed to show much higher reactivity towards ozone, resulting in waters devoid of residual derivatives or persistent toxins, if any when highly polluted waters are treated. In other words, larger and less oxidized organic molecules are expected to show much higher reactivity towards ozone. Here, it is worth mentioning that the oxidation state increases with increasing number of oxygen (or halogens) atoms per atom of carbon. Therefore, if oxalic acid is regarded as being a bottleneck derivative that arise from oxidation of almost all organic compounds, its total mineralization may be regarded as being a major step for achieving total mineralization of any organic molecule. Effective oxidative treatment of bulky molecules such as antibiotics and counterparts is expected to result in waters devoid of residual derivatives or persistent toxins, if any when highly polluted waters are treated. The approach in the present thesis consisted in investigating the degradation of sulfamethoxazole (SMX), $C_{10}H_{11}N_3O_3S$, and of various aromatic pollutants under the same operating conditions as for oxalic acid. The aromatic molecules investigated herein are supposed to behave as SMX derivatives. Comparison between their different degradation pathways will be useful for adapting the operating conditions for each organic substrate and for better understanding why organic pollutant release in nature results in incomplete oxidative treatment that may produce even more hazardous organic pollutants than the parent molecules. The optimum conditions for ozonation differ according to the chemical structure and physicochemical properties

of each organic substrate. One of these properties is the pKa value, which determines the acid-base interactions involved in the adsorption step. This property also governs the contribution of protonation-deprotonation and ion-exchange processes, which is specific according to the polarity and (or) organophilic-organophobic character of each organic molecules. The adsorption of ionic molecules bearing sulfonate and (or) carboxylic groups are supposed to require different pH and catalyst amounts as compared to organophobic substrates. The most important finding of the kinetic studies comparatively through three different analysis methods demonstrates that when rigorously and accurately performed, COD and UV-Vis measurements allow quick and qualitative assessment of the global order and rate constant of the ozonation process for the different organic substrates studied. Notwithstanding their low accuracy, both COD and UV-Vis measurements allowed demonstrating that the 1^{st} order model that supposes a constant ozone concentration imposed by its limited solubility in water is valid only during the first 2 min of ozone. COD and UV-Vis measurements showed this tendency, which was confirmed by HP-ToF-MS. Thus, it clearly appears that ozonation triggers and proceeds through direct reaction with molecular ozone until the adsorption of sufficient amounts of reagent and first intermediates for at most 3-5 min, when another pathway is supposed to be involved. Therefore, it appears that quick qualitative investigation of the evolution in time of the ozonation for a given organic molecule does not necessarily need sophisticated analysis techniques such as HPLC-MS, unless intermediate identification is strongly required. In all cases, since COD measurements are commonly used by engineers in wastewater treatment plants to assess the amount of organic pollutants, their comparison with measurements through different analysis methods was regarded as being judicious and useful for showing the discrepancy between these methods. Identification of the main ozonation intermediates of sulfamethoxazole, 3-hydroxybenzaldehyde, and phenol allowed understanding that aromatic pollutants decompose almost similarly, regardless to their molecular weight. The structure of the

identified intermediates was established based on comparison of their retention times with commercially available standards and their m/z ratio. This was supported by previously reported information (Rodayan *et al.*, 2010; Larcher and Yargeau, 2013; Mar Gómez-Ramos *et al.*, 2011; Azevedo *et al.*, 2006; Liu *et al.*, 2013; Farzadkia *et al.*, 2014; Wang *et al.*, 2012; Santos *et al.*, 2005; Schleinitz *et al.*, 2009; Yang *et al.*, 2010; Poznyak *et al.*, 2006).

The effect of catalyst addition on degradation of organic substrates and COD removal was thoroughly discussed in this chapter. For instance, Fe(II)-Mt addition induced an appreciable but slower COD decrease, as compared to the fast depletion of the UV-Vis bands. Moreover, short required times for total disappearance of an UV-Vis band with Co(II)Mt do not necessarily mean higher activity than Fe(II)Mt, but only different behavior. In addition, the error in the experimental data does not allow clearly distinguishing the cations by their effectiveness in a single measurement. In other words, Co(II)Mt sometimes appears to be more effective, but statistically Fe(II)Mt showed slightly higher performance in most ozonation attempts. Also, regardless to the organic substrate to be degraded, Fe(II)Mt produced higher COD removal in less ozonation times, as compared with non-catalytic ozonation of phenol, taken as reference. Longer ozonation times without solid catalyst showed that COD removal involves a series of successive plateaus. This is likely due to successive steps in the oxidative degradation of a given organic substrate. Each plateau appears to be an induction period involving ozone accumulation up to minimum amount of level to be triggered. One may emphasize that, COD measurements have an error of 2-3%. The slight discrepancy between 98 and 100% COD removal should be rather regarded as a confirmation of the effectiveness of our ozonation test. Therefore, even for longer ozonation times than 30 min, this is still regarded as being an outstanding result, given that an ample literature clearly shows that most total mineralization was achieved around 180 min (Azzouz *et al.*, 2010; Azzouz, 2012; Beltran and al., 2002;

Beltran *et al.*, 2005; Liu *et al.*, 2011; Pines et Reckhow, 2002; Roy *et al.*, 2010; Yunzheng *et al.*, 2003). Some obtained kinetic data may need a detailed explanation. For instance, reaction order (n) <1 is a special feature of surface processes where adsorption and diffusion play significant roles, while n-values higher than unity indicates complex chemical processes. This must be due to a specific behavior of 4-nitrophenol. The most plausible explanation that can be provided so far is that 4-nitrophenol degradation did not obey 1st order kinetics, but rather a constant 0.7 -0.8 order kinetics from the very beginning of the ozonation process and during the whole process, without undergoing any change in the mechanisms pathways (as supported by the high R^2 value). Such a pathway did not seem to depend on ozone solubility (1st order excluded), and should mainly involve a surface process, where adsorption and surface reactions appear to be determining steps more than for the other organic substrates. Investigations are still in progress in this direction. Besides, for some ozonation intermediates of some organic substrates exceptionally $R^2_{\text{n-order}} > R^2_{\text{1st-order}}$. Based on the fact higher R^2 values correspond to the most probable kinetic model, this question may be answered in the same manner as previously. In other words, the n-order is more probable for some cases where ozonation is either strongly depending on the ozone concentration or involved in complex reaction pathways. It is worth mentioning that, the rate constants were calculated for successive intervals in time as being proportional to the average concentration of the organic substrate in lieu of the instant value, which can be used only for an infinitesimal time interval. This average concentration of the organic substrate was expressed in terms of average relative absorbance for a given UV-Vis band ($A_{r,med}$) or average residual COD ($COD_{r,med}$).

5. Chapter 5 which is a global Conclusion: this section not only gathers the main conclusions made at the different steps of this research, but also provides a deep analysis of them. Most of these conclusions allow validating the hypotheses considered for tackling the issue related to organic pollutant mineralization and for

adopting this approach which considers that total elimination of a bottleneck derivative is a necessary step for achieving total mineralization of the parent organic substrate. Knowledge advancement in the total mineralization of organic pollutants by clay-catalyzed ozonation was the main target of this thesis. This research is expected to provide valuable findings for further improvements regardless to the water to be treated (drinking water or wastewater treatment). The determination of the optimum conditions to achieve total mineralization of a typical refractory short-chain derivative such as oxalic acid allows assessing the relative reactivity towards ozone of various organic molecules that differ by their size and structure. These molecules are representative of the main pollutant families in most wastewaters. This plan was conceived to highlight the role of clay-based catalysts for addressing the issue of low solubility and short lifetime of ozone, through the major contribution of adsorption via Lewis acid-base interactions. However, care should be taken when dealing the involvement of adsorption, which does not necessarily mean the retention of high amounts of reagents by the catalyst, but rather optimum quantities that promote the catalytic act, without blocking the desorption of the ozonation products. Therefore, the contribution of adsorption to the assessment of the instant decrease in concentration is fairly negligible, as supported by periodical analysis through FTIR and X-ray fluorescence of the catalyst in the absence of ozone. Therefore, the value of removal yield was evaluated within the accuracy range of the respective analysis method. Only traces of organic compounds (sulfamethoxazole, aromatics substrates, and short chains acids) have been detected over clay-based catalysts. Higher but still low amounts of adsorbed non-acidic organic substrates were detected on mesoporous silicates, such as Santa Barbara Amorphous (SBA) and Mobil Crystalline Material (MCM), due to their higher organophilic behavior. These data have already been submitted for publication. Unlike SBA silica, clay catalyst have exchangeable cations (Lewis acidity), whose mobility according to the pH level is expected to promote chelation processes by the available electron pair (Lewis basicity) of the organic

substrates, if any. However, Lewis acid-base interactions are restricted only to S and N-containing organic substrates, and more particularly oxygenated molecules. The latter usually appear after 2-3 min of ozonation. This is in agreement with our kinetic studies, which revealed changes in the 1st order kinetics once ozonation is triggered. Fe(II)Mt catalyst analysis through XRF after 5-10 min ozonation showed a slight increase in the amount of carbon atoms, which account for less than 1 wt. % of the instant concentration measured. The average error in assessing the instant removal yield is around 2-3% even by HPLC-ToF-MS.

The samples analyzed by HPLC-ToF-MS methods originated from batches of 20 to 100 mL of aqueous solution of the organic substrate used for ozonation attempts with a 6 $mg.min^{-1}$ ozone throughput. Our calculations gave ozone concentration ranging from 300 $mg.L^{-1}$ to 60 $mg.L^{-1}$. It is worth mentioning that, lower ozonation concentration did not produce total mineralization with reasonable reaction times. This was the main argument that justifies the use of such an ozone concentration. Another argument resides in the fact that lower ozone concentration produces low amounts of derivatives difficult to be accurately determined even through HPLC-ToF-MS analysis. The ozone generator produces a constant amount of 6 mg ozone per minute, which can be easily converted in ozone dose. Obviously, this ozone concentration imposes a certain evolution in time of the ozonation process. This device was purchased according to our specific requirements. Nevertheless, certain information relative to the evolution in time of the ozonation process will be lost. Obviously, such an evolution in time strongly depends on the ozone concentration, but for a given concentration, the use of ozone dose will not allow observing changes in time of the ozonation pathway. Other experimental details are provided in the supplementary files of supporting information of the papers published and in the appendices to the present manuscript. Throughout the entire manuscript in the present thesis, whose chapters 2-4 are the exact contents of the three papers published. Here,

it should be noticed that all figures of these supplementary files were included in these appendices, which were cited in the text through the corresponding figures and tables. Also, it is worth mentioning that in the whole thesis manuscript, there is no figure taken from the literature and all figures are designed by me, sometimes being helped by my professors. The most important objective of the present thesis was to demonstrate that natural and widely available clay materials can be conveniently used for obtaining low cost catalysts for sustainable water treatment routes that do not produce sludges or any other residues. It must be reminded that there are no lower cost catalysts than those obtained from clay minerals, which do not need sophisticated synthesis procedures. In addition, in our opinion the other oxidative methods tested so far throughout the world are not necessarily cheaper than the catalytic ozonation. The fact that oxalic acid, for instance, can be thoroughly mineralized after at most 20-25 min, versus 3 hours and even more with other oxidative treatments, should regarded as the best justification of such a statement. Now, a question still remains to be answered, namely: Is ozone production during 20-25 min more expensive than artificial light exposure for much longer photoreaction time? The response to this question depends on many factors, among which reduction of excess ozone that does not participate to the reaction still remains a major issue to be addressed. Attempts to improve ozone solubility and/or adsorption on a solid surface are interesting research directions. Since adsorption plays a key role, higher ozonation effectiveness requires higher specific surface area (SSA). In this regards, encouraging results were obtained with SBA-like silica, which display SSA value of 700-1000 $m^2.g^{-1}$. These results have been recently submitted for publication in a high impact factor journal. In all cases, catalytic ozonation in the presence of low cost clay based catalysts has major advantages such as fast and effective mineralization without water contamination with catalyst, without major investments and bulky plants for water treatments.

REFERENCES

Azevedo, E. B., Radler de Aquino Neto, F. and Dezotti, M. (2006). Lumped kinetics and acute toxicity of intermediates in the ozonation of phenol in saline media. *Journal of Hazardous Materials*, B128, 182–191.

Azzouz , A. (2012). Advances in oxidative decomposition of oxalic acid in aqueous media, in: J. C. Taylor (Eds.), Advances in chemistry research (p. 1 – 31). New York :Nova-Publishers.

Azzouz, A., Kotbi, A., Niquette, P., Sajin, T., Ursu, A.-V., Rami, A., Monette, F. and Hausler, R. (2010). Ozonation of oxalic acid catalyzed by ion-exchanged montmorillonite in moderately acidic media. *Reaction kinetics mechanisms and catalysis*, 99, 289 – 302.

Beltran, F.-J., Rivas, F.-J., Fernandez, L.-A., Alvarez, P.-M. and Montero-de-Espinosa, R. (2002). Kinetics of catalytic ozonation of oxalic acid in water with activated carbon. *Industrial & Engineering Chemistry Research,* 41, 6510–6517.

Beltran, F.J., Rivas, F.J. and Gimeno, O. (2005). Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water. *Journal of Chemical Technology and biotechnology*, 80, 973–984.

Can, Z.S. and Gurol, M. (2003). Formaldehyde formation during ozonation of drinking water, *Ozone: Science and Engineering*, 25, 41 – 51.

Canton, C., Esplugas, S. and Casado, J. (2003). Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light. *Applied Catalysis B: Environmental*, 43, 139–149.

Cooper, C. and Burch, R. (1999). An Investigation of catalytic ozonation for the oxidation of halocarbons in drinking water preparation. *Water Research*, 33, 3695 – 3700.

Daud , N.K., Ahmad , M.A. and Hameed , B.H. (2010). Decolorization of acid Red 1 dye solution by Fenton-like process using Fe–Montmorillonite K10 catalyst. *Chemical Engineering Journal*, 165, 111–116.

Diez, M.C. (2010). Biological aspects involved in the degradation of organic pollutants. *Journal of plant Nutrition and Soil Science,* 10, 244 – 267.

Elsousy, K., Hussen, A., Hartani, K. and Elaila, H. (2007). Elimination of organic pollutants using supported catalysts with hydrogen peroxide. *Jordan Journal of Chemistry*, 2, 97 – 103.

Farzadkia, M., Dadban Shahamat, Y., Nasseri, S., Mahvi, A. H., Gholami, M. and Shahryari, A. (2014). Catalytic ozonation of phenolic wastewater: Identification and toxicity of intermediates. *Journal of Engineering*, http://dx.doi.org/10.1155/2014/520929.

Giordano, G., Perathoner, S., Centi, G., De Rosa, S., Granato, T., Katovic, A., Siciliano, A., Tagarelli, A. and Tripicchio, F. (2007). Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts. *Catalysis Today* 124, 240–246.

Guo, Y., Yang, L., Cheng, X. and Wang X. (2012). The Application and reaction mechanism of catalytic ozonation in water treatment. *Journal of Environmental and Analytical Toxicology,* 2, 1–6.

Henry, M.T. and Beaudry, J.P. (1984). Chimie des Eaux, (p. 56 – 81). Sainte – Foy : Le griffon d'argile Inc.

Ito, H., Kotake, T. and Masai, M. (1996). In vitro Degradation of oxalic acid by human feces. *International Journal of Urology*, 3, 207–211.

Kasprzyk-Hordern , B., Ziolek, M. and Nawrocki, J. (2003). Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Applied Catalysis B: Environmental,* 46, 639–669.

Khankhasaeva, S.T., Bryzgalova, L.V., Dashinamzhilova, E.T. and Ryazanttsev, A.A. (2004). Fe-Montmorillonites in the reaction of organic dyes oxidation. *Chemistry for Sustainable Development,* 12, 713 –717.

Kjellström, T., Lodh, M., McMichael, T., Ranmuthugala, G., Shrestha, R. and Kingsland, S. (2006). Disease control priorities in developping countries, (p. 817 – 833). Washington DC: oxford university press.

Koohestanian, A., Hosseini, M. and Abbasian, Z. (2008). The separation method for removing of colloidal particles from raw water. *American-Eurasian journal of agricultural and environmental*, 4, 266 – 273.

Kumar, P. and Sathyamurthy, N. (2013). An ab initio quantum chemical investigation of the structure and stability of ozone-water complexes. *Chemical Physics*, 415, 214 – 221.

Kwong, C.W., Chao, C. Y., Hui, K.S. and Wan, M. P. (2008). Removal of VOCs from indoor environment by ozonation over different porous materials. *Atmosphetic Environment*, 42, 2300–2311.

Larcher, S. and Yargeau, V. (2013). The effect of ozone on the biodeg radation of 17 α - eth inylestradiol and sulfamethoxazole by mixed bacterial cultures. *Applied Microbiology and Biotechnology*, 97, 2201– 2210.

Legube, B. and Karpel Vel Leitner, N. (1999). Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catalysis Today,* 53, 61–72.

Li, Y.F., Scholtz, M.T. and Van Heyst, B.-J. (2012). Global gridded emission inventories of α-hexachlorocyclohexan. *Journal of Geophysical Research*, 105 (D5), 6621–6632.

Liu, Z.-Q., Ma, J., Cui, Y.-H., Zhao, L. and Zhang, B.-P. (2011). Factors affecting the catalytic activity of multi-walled carbon nanotube for ozonation of oxalic acid. *Separation and Purification Technology*, 78, 147–153.

Liu, Y., Zhu, Y., Xu, J., Bai, X., Zong, R. and Zhu, Y. (2013). Degradation and mineralization mechanism of phenol by $BiPO_4$ photocatalysis assisted with H_2O_2. *Applied Catalysis B: Environmental,* 142– 143, 561– 567.

Mantzavinos, D. (2003). Removal of benzoic acid derivatives from aqueous effluents by the catalytic decomposition of hydrogen peroxide. *Institution of Chemical Engineers,* 81, 99 – 106.

Mar Gómez-Ramos, M., Mezcua, M., Agüera, A., Fernández-Alba, A. R., Gonzalo, S., Rodríguez, A. and Rosal, R. (2011). Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution. *Journal of Hazardous Materials,* 192, 18–25.

Mohan, S. M. (2014). Use of naturalized coagulan ts in removing laundry waste surfactant using vario us unit processe s in lab-scale. *Journal of environmental Management*, 136, 103 – 111.

Munter, R., Trapido, M., Veressinina, Y. and Goi, A. (2006). Cost Effectiveness of Ozonation and AOPs for Aromatic compound removal from Water: A preliminary Ssudy. *Ozone: Science and Engineering* , 28, 287–293.

Negrel, P., Blessing, M., Millot, R., Giraud, E.P. and Innocent, C. (2012). Isotopic methods give clues about the origins of trace metals and organic pollutants in the environment. *Trends in Analitical Chemistry*, 38, 143 – 153.

Nidheesh , P.V. and Gandhimathi, R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination* , 299, 1 – 15.

Numata, M., Yarita, T., Aoyagi, Y., Yamazaki, M. and Takatsu, A. (2005). Investigation of saponification for determination of polychlorinated biphenyls in marine sediments. *Chemosphere,* 58, 865–875.

Pines, D.-S. and Reckhow, D.-A. (2002). Effect of Dissolved Cobalt(II) on the Ozonation of Oxalic Acid. *Environmental Science & Technology,* 36, 4046–4051.

Poznyak, T., Tapia, R., Vivero, J. and Chairez, I. (2006). Effect of pH to the decomposition of aqueous phenols mixture by ozone. *Journal of the Mexican Chemical Society,* 50, 28–35.

Rahni , M. and Legube, B. (1996). Mechanism of salicylic acid precipitation by Fe(III) coagulation. *Water Research*, 30, 1149 – 1160.

Ramirez, J.H., Vicente, M.A. and Madeira, L.M. (2010). Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment. *Applied Catalysis B: Environmental*, 98, 10–26.

Ren, L., Li, G., Han, Y.C., Jiang, D.H and Huang, H.C. (2007). Degradation of oxalic acid by Coniothyrium minitansand its effects on production and activity of β-1,3-glucanase of this mycoparasite. *Biological Control*, 43, 1–11.

Rice, R. G., Netzer, A. and Arbor, A. (1982). Hand book of ozone technology and application (p. 255 – 285). Michigan : Science publishers.

Rodayan, A., Roy, R. and Yargeau, V. (2010). Oxidation products of sulfamethoxazole in ozonated secondary effluent. *Journal of Hazardous Materials,* 177, 237–243.

Roy, S., Vashishtha, M. and Saroha, A.-K. (2010). Catalytic Wet Air Oxidation of Oxalic Acid using Platinum Catalysts in Bubble Column Reactor: A Review. *Journal of Engineering Science and Technology Review*, 3, 95-107.

Santos, A., Yustos, P., Cordero, T., Gomis, S., Rodriguez, S. and Garcia-Ochoa, F. (2005). Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization. *Catalysis Today*, 102–103, 213–218.

Schleinitz, K. M., Schmeling, S., Jehmlich, N., Bergen, M., Harms, H., Kleinsteuber, S., Vogt, C. and Fuchs, G. (2009). Phenol degradation in the strictly anaerobic iron-reducing bacterium geobacter metallireducens. *Applied and Environmental Microbiology,* 75, 3912–3919.

Stuber, F., Font, J., Fortuny, A., Bengoa, C., Eftaxias, A. and Abregat, A. (2005). Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater. *Topics in Catalysis*, 33, 3 –50.

Wang, C. M., Lai, T. L., Chiou, J. Y. Z., Ho, K. F., Shu, Y. and Wang, C. B. (2012). Degradation of phenol over nickel oxides: Influence of the preparation routes, Asia Pacific Conference on Environmental Science and Technology. *Advances in Biomedical Engineering*, 6, 515 – 521.

Wang, D. and Fiessel, W. (2008). Evaluation of media for simultaneous enumeration of total coliform and Escherichia coli in drinking water supplies by membrane filtration techniques. *Journal of Environmental Science*, 20, 273–277.

Yang, L. P., Hu, W.-Y., Huang, H. M. and Yan, B. (2010). Degradation of high concentration phenol by ozonation with ultrasonic irradiation. *Desalination and Water Treatment*, 21, 87–95.

Yunzheng, P., Ernst, M. and Schrotter, J.-C. (2003). Effect of phosphate buffer upon CuO/Al_2O_3 and Cu (II) catalyzed ozonation of oxalic acid solution. *Ozone: Science and Engineering,* 25, 393–397.

CHAPTER II

ADVANCES IN CATALYTIC OXIDATION OF ORGANIC POLLUTANTS - PROSPECTS FOR THOROUGH MINERALIZATION BY NATURAL CLAY CATALYSTS

Abstract

This chapter is devoted to oxidative water treatments, with emphasis on catalytic ozonation. The approach tackled herein resides in highlighting the main findings from a wide variety of oxidative treatments, which can be useful for envisaging improvements towards total mineralization of organic pollutants. Comparison between operating conditions for specific pollutant-catalyst-oxidizing agent systems is quite difficult, and was not targeted in the present work. However, when deeply and judiciously analyzed, such a comparison allows demonstrating that, except for some works, most of these attempts seldom took into accounts basic requirements such as the parameter interactions, the role of cation mobility around a solid surface, if any, the multiple pollutant-catalyst-oxidizing species interactions and the significant contribution of adsorption, etc. Otherwise, how to explain that many experiments are still conducted with unsuitable catalysts under totally inadequate operating conditions? A better understanding of the essential requirements for a catalyst to achieve total mineralization of any organic molecules is the main objective of this work

The data summarized herein allow devoting a special interest to ozone. In spite of its low solubility in water,ozone is a powerful oxidizing agent and probably the easiest to handle, being produced in-situ by non cumbersome devices. The use of catalysts is an ultimate strategy to improve the ozonation performance, by reducing the Chemical Oxygen Demand (COD), even until total disappearance. However, solid catalysts, more particularly those developing high specific surface areas, such as silicates, aluminosilicates, zeolites, pseudozeolites, and clay minerals and derivatives, are expected to display appreciable performances in ozonation. The latest findings show strong dependency of their catalytic activity on the chemical and physical characteristics of their surface, their concentration in the liquid media, the pH level of the reaction mixture and other parameters. The effects of these factors will be systematically examined in this review paper. The state-of-the-art in the catalytic ozonation of organic pollutants may be useful to understand the contribution of both surface and bulk ozonation reaction in the vicinity of the surface of a solid catalyst, and more particularly the role of the catalytic agent and the mobility near the solid surface. A rigorous data synthesis, made available in the present paper, allows understanding the ozone scavenging by the very species present in water, and correlating the highest effectiveness of ozone in the presence of a solid catalyst with optimum pH and catalyst concentration. The latter suppose strong interactions between the main factors, which remain to be elucidated for each type of catalyst.

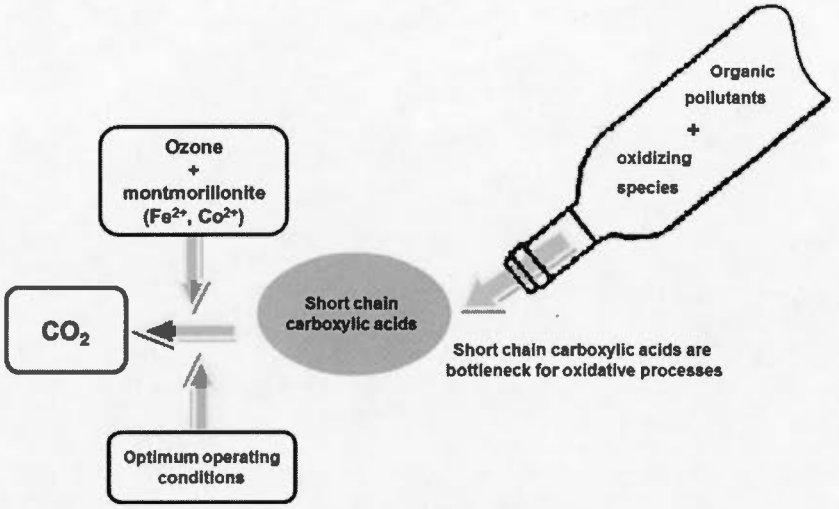
The structure of this review paper makes emphasis on montmorillonite, which exhibits most of the required properties for effective ozonation catalysts. These are common features of natural clay minerals and zeolites, which appear as interesting candidates for large-scale water treatments, targeting complete mineralization of organic pollutants without generating persistent toxins.

2.1 Introduction

Water pollution remains a major issue to be addressed by improving wastewater treatments not only from conventional industries but also for novel eco-designed technologies to be implemented. Among the different water treatment methods tested so far, oxidative techniques are undoubtedly the most promising routes when total mineralization of organic pollutants is targeted. There exists a wide variety of oxidative techniques such as Fenton and photo-Fenton processes, ozonation and catalytic ozonation, photocatalysis in the presence of hydrogen peroxide with, for example titanium dioxide, radiolysis, electrochemical oxidations and various combinations of some of these procedures. Regardless to their efficiency, all these techniques have a common feature that resides in the unavoidable formation of harmful by-products in the case of incomplete decomposition of the organic substrates

Among these, catalytic ozonation is one of the most effective and eco-friendly water treatment methods (Munter *et al.*, 2006). Ozone is a powerful oxidizing agent that may lead to complete mineralization of organic $C_xH_yO_z$ compounds into carbon dioxide under specific operating conditions (Zhao *et al.*, 2009; Daud *et al.*, 2010), sulfate and nitrate anions when S and N atoms are also present. This allows envisaging potential applications in industrial processes (Guo *et al.*, 2012). Nonetheless, ozone is characterized by a short lifetime and low solubility in aqueous media. These are major drawbacks that reduce considerably the contact time in water and interaction with the organic substrates to be decomposed. Ozone alone often results in incomplete degradation of the organic substrate (Guo *et al.*, 2012), and, paradoxically, even acts a potential source of toxic intermediates. Significant improvements can be brought by using solid catalysts, which are also supposed to

favor adsorption, prolonging thereby the contact time in the liquid media. Solid catalysts displaying high specific surface area could be of great benefit for



Scheme 2.1. Effective strategy for total mineralization of organic contaminants

wastewater treatments aiming to total decomposition of organic contaminants without generating persistent by-products (Scheme 2.1). This could be regarded as an interesting route to explore.

Nowadays ozonation methods are routine technologies in wastewaters treatment, more particularly in some European countries (Legube and Karpel Vel Leitner, 1999; Wu *et al.*, 2008). Ozone has promising prospects in wastewater treatment, because it can be easily produced from air by means of compact and small volume devices that operates at ambient pressure and temperature (Fontanier *et al.*, 2005). According to numerous references, in small concentration not exceeding 5-50 ppm for exposure times ranging from 30-60 min, ozone is not hazardous for human health and can be simply handled. In addition, it can readily decompose into harmless compounds (oxygen and water). Because, different ozone dosages are involved for treating

different types of wastewaters, an optimum use of ozone requires a minimum knowledge on the origin and the emission source of the wastewaters to be treated. This implies that effective oxidative treatment needs sufficient data on the chemical composition of the effluents and the nature of the organic pollutants to be decomposed.

A wide variety of hazardous compounds that may cause human diseases such as neurological disorders, cardiovascular disease and diarrheal diseases (Kjellström *et al.*, 2006) can be eliminated by wet oxidative treatments at ambient temperature, unlike incineration methods which produce toxic emission flues (Munter, 2001; Beltran *et al.*, 2005; Negrel *et al.*, 2012; Nidheesh and Gandhimathi, 2012; Elsousy *et al.*, 2007; Giordano *et al.*, 2007). Wet oxidative treatments are confronted to a hard challenge, inasmuch as the maximum permissible concentration of some persistent organic compounds and dyestuffs in some wastewaters is much less than 1 ppm, while the outlet concentration from chemical plants is often several times higher than the allowed threshold (Ramirez *et al.*, 2010; Mantzavinos, 2003; Khankhasaeva *et al.*, 2004; Li *et al.*, 2012). Even other attempts through biological and physical water decontamination from organic pollutants turned out to be unsatisfactory as compared advanced oxidative processes (AOPs) (Diez, 2010; Ito *et al.*, 1996; Ren *et al.*, 2007; Azzouz, 2012; Wang and Fiessel, 2008).

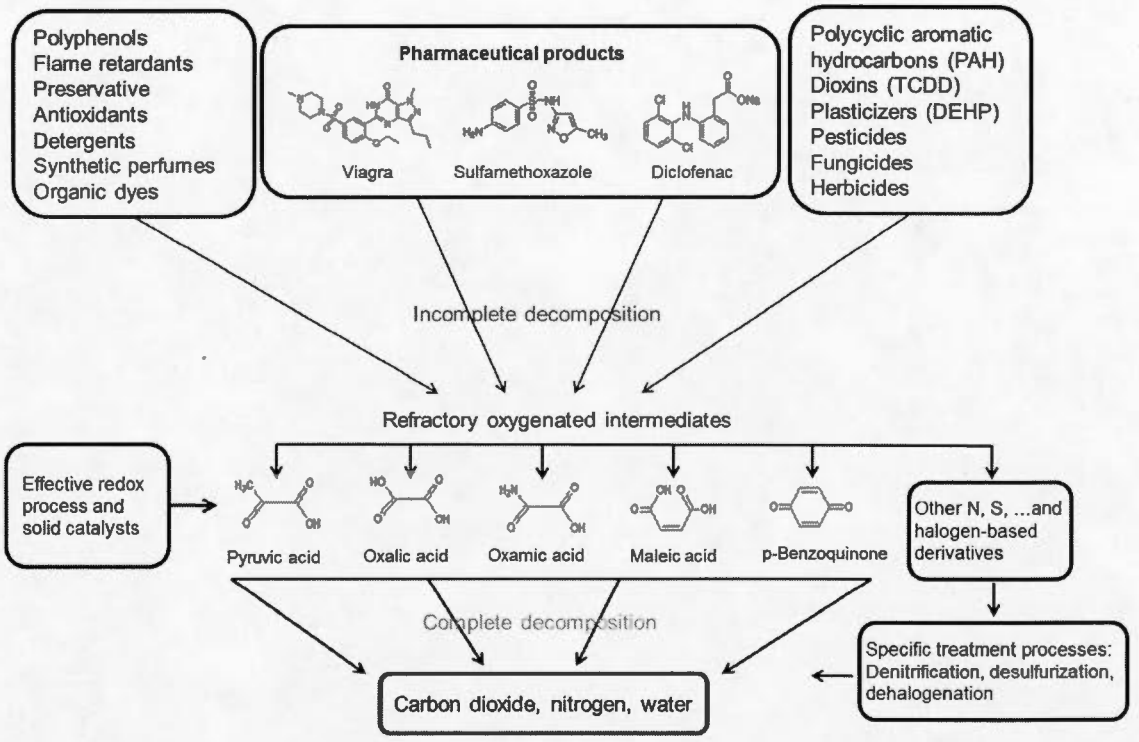
2.2 Water pollution by organic compounds

Wastewaters contain a wide variety of chemical compounds such as organic pollutants, eutrophication agents (nitrates, phosphates), metal cations and others (Scheme 2.2). Such diversity requires different approaches in wastewater treatments, and a special interest is focused herein to organic pollutants. Their common features

reside in their high reactivity towards oxidizing agents, more particularly to ozone, in spite of their different physico-chemical nature.

Major organic pollutants arise from chemical and pharmaceutical industries, food technologies, oil refineries, petrochemical plants, dye and textiles manufacturing units, agro-industrial activities and others. Petrochemical wastewaters often contain oils and grease, phenols, aromatics and chlorinated organic compounds such as dioxins. Paper and pulp mills, sugar mills, and leather tanneries are other important emission sources of organic pollutants (Daud *et al.*, 2010; Kjellström *et al.*, 2006). Organic wastes originating from industrial and urban sewages also contain hazardous compounds such as aromatic hydrocarbons, petroleum products, halogenated solvents, herbicides like 2,4-dichlorophenoxyacetic acid, detergents, phenols and derivatives, antibiotics, estrogens, contraceptives, and require treatments before being released in soils, rivers and seas (Munter, 2001; Beltran *et al.*, 2005; Negrel *et al.*, 2012; Nidheesh and Gandhimathi, 2012; Elsousy *et al.*, 2007; Giordano *et al.*, 2007; Ramirez *et al.*, 2010).

Phenolic compounds are an important family of wastewater polluting agents. They usually arise from chemical industries for the manufacture of pesticides, pharmaceuticals, synthetic dyes (Nidheesh and Gandhimathi, 2012), fuel additives (Elsousy *et al.*, 2007), and food-processing industries, more particularly from olive oil and wine producing plants around the Mediterranean (Giordano *et al.*, 2007; Mantzavinos, 2003). They may also originate from incomplete oxidative treatments of a wide variety of organic pollutants.



Scheme 2.2. Main sources of organic contaminants and oxidative degradation strategy.

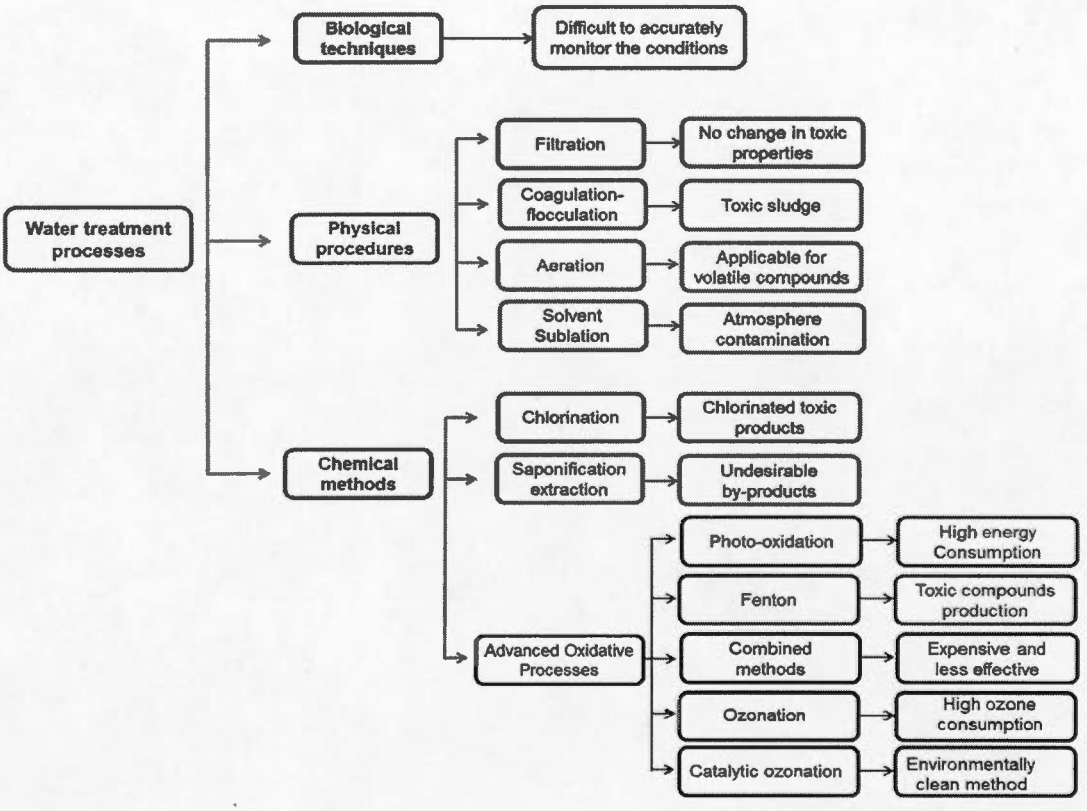
Organic dyes, more particularly of azo type, are also released in wastewaters; most of them show carcinogenic, mutagen, and allergic effects for living organisms. Such compounds are difficult to remove through physical treatment methods, and only oxidative decolourization of the corresponding wastewaters can be considered (Khankhasaeva *et al.*, 2004). However, care should be taken in the case of incomplete oxidation, because traces of hazardous derivatives may be generated. The latter are usually regarded as being persistent organic pollutants (POP).

Polyaromatic hydrocarbons (PAHs) are a class of high molecular weight organic compounds with three or more phenyl rings, including bicyclic compounds such as naphthalene and biphenyl (Li *et al.*, 2012). Such compounds are regarded as being

particularly toxic, and unless thermally decomposed into heavy asphalt compounds, they usually generate phenolic compounds upon oxidative treatment. That is being said, as previously stated, each organic pollutant family requires specific elimination methods. The latter should be judiciously chosen by imposing minimum traces of residual organic pollutant and derivatives, if any, as the main criterion. Obviously, this supposes that previous constraints related to energy consumption and CO_2 emission considerations are satisfactorily taken into accounts.

2.3 Removal of suspended and dissolved organic compounds

The dispersion state of the organic pollutants in the liquid media is a key-factor in applying adequate elimination techniques for a given family of organic compounds. For instance, suspended organic compounds can be conveniently separated from wastewaters by different scale filtrations and settling, while emulsified or dissolved organic compounds may be removed by either through precipitation, solvent extraction or oxidative methods (Scheme 2.3). According to the type of organic contaminant to be removed, physical procedures involved adsorption, coagulation and (or) flocculation, or even biological procedures may be applied for wastewater remediation.



Scheme 2.3. Main approaches for organic pollutant elimination.
Here, each type of treatment has specific efficiency for specific purposes, and no objective comparison can be made without similar criteria. However, for the specific objective of this research, AOPs and more particularly, catalytic ozonation appear a being the most convenient and promising routes, notwithstanding the initial investment costs.

2.3.1 Conventional techniques for water treatments

Biological treatment using micro-organisms has long been used to eliminate eutrophication agents and pollutants. Fungal and bacterial degradation of organic compounds is known as bioremediation. Fungi were already found to convert pesticides into nontoxic derivatives, which are further degraded by bacteria (Diez, 2010). Reportedly, Oxalobacter formigenes, an anaerobic bacterium isolated from human feces has the ability to degrade oxalic acid (Ito *et al.*, 1996), and appreciable

mineralization levels were achieved using Coniothyrium minitans fungus or brown rot fungus (Ren *et al.*, 2007; Azzouz, 2012). In spite of these performances, bioremediation processes are often pH-dependent and fairly difficult to be accurately monitored. Appreciable fluctuations in their activity due to frequent contaminations with other competitive micro-organisms may affect the process efficiency.

In physical procedures, the dispersed contaminant in both liquid (solution or emulsion) and solid state (suspension) is separated from the liquid media without changes in chemical structure. Such methods are usually applied for removing highly polluted wastewaters, and have almost no efficiency when dealing with complete purification into drinking water. When applicable, microstraining is undoubtedly one of the most important physical water treatments, which involves separation via filtration of small particles (Wang and Fiessel, 2008). This method uses of entangled wires made of stainless steel or polymers as filters with aperture size of only 60-70 μm. Other similar procedures developed so far, utilize membranes and other separating systems. In the case of very fine particles, a previous coagulation-flocculation process is employed to increase the particle size through the formation of flocks.

Coagulation, alone or combined to other methods, is usually employed to alter a colloidal state by modifying the surface charge of the suspended particle. An almost similar process is involved with an emulsion of liquid micro-droplets. For this purpose, coagulating agents such as alum [$Al_2(SO4)_2 \bullet 18H_2O$], $FeCl_3$, $FeSO_4$ are commonly employed (Wang and Fiessel, 2008; Koohestanian *et al.*, 2008). Devoid of their solvation layer, the latter can adhere to each other into bulkier and heavier aggregates (flocks). The latter are prone to a settling step, and the residual suspension being removed through filtration of the supernatant (Mohan, 2014; Rahni and Legube, 1996).

Pollutant capture through adsorption on a solid surface is the most commonly used physical technique for removing dissolved compounds. However, this technique should be limited to wastewaters weakly loaded in contaminants and as long as adsorbent saturation is not attained. The adsorbent effectiveness is directly related to the extent of the surface area available for interaction with the contaminant molecules. A classical adsorbent with high affinity towards organic compounds is undoubtedly porous carbon (activated carbon, fullerenes, carbon nanotubes, etc.) (Kwong *et al.*, 2008). Nanostructured carbons can display surface area of 1000 $m^2 .g^{-1}$ and even beyond. Activated carbon is the most affordable carbon-based material from the production cost viewpoint, and acts as an effective adsorbent for a wide variety of organic substrates (Ramirez *et al.*, 2010; Mohan, 2014; Kasprzyk-Hordern *et al.*, 2003; Henry and Beaudry, 1984, p. 56-81; Stuber *et al.*, 2005).

Solvent sublation or commonly ''solvent extraction'' is a conventional treatment for highly polluted aqueous wastewaters. In this separation technique, the dissolved organic compound is transferred and concentrated at the top of a column filled with an organic solvent by means of ascendant micro bubbles of air. This method turned out to be more effective than the aeration methods, because it prevents the organic contaminant to re-disperse into the aqueous phase. In addition, unlike the aeration methods, solvent sublation can also eliminate non-volatile pollutants (Bayati *et al.*, 2009). The evaporation of the organic contaminant into the air stream during the aeration treatment can be achieved by increasing the liquid-gas interface. For this purpose, bubbling large amounts of air through the wastewater bulk causes air and water to disperse into a mixture of fine bubbles and very small droplets (Zhang *et al.*, 2014; Liu *et al.*, 2012; Nollet, 2007, p. 300 – 302). The efficiency of such physical methods is however limited by the transfer velocity of the contaminant through the liquid-liquid (sublation) or liquid-gas interface (aeration). The main drawback of

such a water treatment technique is the use of organic solvents, which unavoidable results in traces of organic molecules. That is why even the most performing devices cannot produce total elimination of the organic substrates from the treated wastewaters.

Another route involves the use of chemical methods, i.e. the decomposition of organic compounds into products with different chemical structures. An essential requirement for such wastewaters treatments resides in achieving weakly endothermal chemical reactions. The latter should use powerful oxidizing or reducing agents in order to avoid heating and the production of residual amounts of harmful products and hazardous derivatives. Here, a special interest is devoted to those treatment processes that do not involve fossil energy consumption and greenhouse gas emissions. Such degradation reactions should also show fast kinetics and high conversions. When such requirements are not fully satisfied, improvements can be brought by using suitable catalytic systems, but, in most cases, the operating conditions have to be optimized in correlation with the catalyst features. For instance, polychlorinated biphenyls (PCBs) are an important kind of persistent organic pollutants, which can be degraded by saponification, but the reaction is more efficient upon heating (Numata *et al.*, 2005). PAHs may also be removed by saponification, but the reaction mixture was found to still contain undesirable by-products even under reflux at 95°C (Northcott and Jones, 2003). For such decomposition processes, the needs for heating are major shortcomings, which limit their applications for large-scale batches.

Theoretically, the presence of carbon atoms in their structure makes that all organic molecules are able to react with oxygen and oxidizing agents. The most commonly employed oxidizing agents are permanganate and hypochlorite anions, hydrogen peroxide or ozone. A wide variety of oxidative decomposition processes have been

developed until now, among which chlorination has even been employed in industrial facilities for wastewater treatments. Nevertheless, such techniques are progressively losing interest, because of the unavoidable formation of chlorinated derivatives and by-products.

2.3.2 Oxidative processes for total mineralization

Oxidative procedures targeting total mineralization of organic pollutants into harmless final products, more particularly the so-called Advanced Oxidative Processes (AOP) have particularly attracted attention. The most important AOPs may be classified as follows (Kasprzyk-Hordern *et al.*, 2003):

a. Fenton processes (using the H_2O_2/Fe^{2+} combination as the Fenton's reagent);
b. Ozonation-peroxidation combination (O_3/H_2O_2);
c. Photo-oxidation processes: (O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV);
d. Catalytic photo-ozonation: (catalyst/O_3/UV);
e. Catalytic ozonation: catalyst/O_3.

Regarded as being environmentally clean treatments of wastewaters, they are still prone to intensive investigations. When applied to oxygenated organic contaminants that do not contain heteroatoms such sulfur or nitrogen, effective AOPs should generate CO_2 and H_2O as the final products. Depending on the structure of the organic molecules, oxides of other chemical elements are also produced, but, in this case, special consecutive water treatments are needed. In most AOPs, the main oxidizing agent is the hydroxyl free radical ($^{\bullet}OH$), more particularly in alkaline media. This radical is even more reactive than chlorine, permanganate and hydrogen peroxide, being a non-selective oxidizing species that readily and rapidly reacts with a wide variety of organic substrates (Munter, 2001; Elsousy *et al.*, 2007; Wang and

Fiessel, 2008). Most AOPs involve a direct attack of hydroxyl radicals on the organic molecules yielding organic radicals and water (Reaction 2.1) (Stasinakis, 2008):

$$R\text{-}H + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \qquad (2.1)$$

In this reaction, C=C compounds are more reactive towards $^{\bullet}OH$ radical attack than saturated molecules, and the reactivity towards oxidative species decreases with decreasing molecular weight and increasing oxidation level. This explains why partially oxidation of organic molecules generates smaller size derivatives, usually oxalic acid and short chain intermediates, which display lower reactivity towards oxidation than their parent molecule. The latter usually accumulate as the final products, because they are known to be quite refractory even to the most reactive oxidizing species. Catalytic oxidation of organic pollutants may produce total mineralization into CO_2 and water, but only in optimum amounts of catalyst and oxidizing agent, pH and concentrations of the organic substrate (Shivaraju, 2011). Catalytic oxidation of organic molecules containing sulfur, nitrogen and (or) other heteroatoms is expected to generate also nitrate and sulphate anions.

At ambient temperature and pressure, oxidative processes generate sufficient $^{\bullet}OH$ radicals to oxidize the major part of the organic compounds present in polluted water (Stasinakis, 2008; Tizaoui *et al.*, 2008; Iurascu *et al.*, 2009; Pang *et al.*, 2011), but such radicals show limited efficiency, more particularly in flow water treatment, due to their extremely short lifetime.

One of the most conventional oxidative methods is the Fenton process (Nidheesh and Gandhimathi, 2012), which displays highest efficiency around pH 3, due to the preponderance of Fe^{2+} cation at the expense of its ferric counterpart (Fe^{3+}). Here, the [Fe^{2+}/ H_2O_2] ratio, H_2O_2 concentration, temperature, initial concentration of the

pollutant, and, more particularly pH are expected to play key roles. Increasing pH was found to be detrimental because it reduces the amount of Fe^{2+} cations via precipitation. This is expected to attenuate the conversion of hydrogen peroxide into $^{\bullet}OH$ radicals (Reaction 2.2) (Barbunsinski, 2009):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2.2)$$

The major shortcoming of such a process may be a source of water contamination, because exhaustive $^{\bullet}OH$ production requires appreciable Fe^{2+} concentrations of 50-80 ppm, while the maximum level allowed in treated wastewaters is only 2 ppm. Another drawback is that high Fe^{2+} concentrations require continuous pH adjustments that raise the operating costs in wastewater treatments (Ramirez *et al.*, 2007). Besides, the H_2O_2 amount should be rigorously monitored to avoid $^{\bullet}OH$ radical scavenging even by hydrogen peroxide, resulting in less reactive species such as $HO_2^{\bullet}$ (Reaction 2.3) (Daud *et al.*, 2010; Ramirez *et al.*, 2010; Flores *et al.*, 2008):

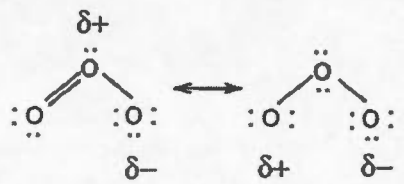
$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \qquad (2.3)$$

Photo-catalytic oxidation of organic substrates was found to produce higher performances when using solid catalysts such as TiO_2 in its anatase form, metal oxides and sulfides such as α-Fe_2O_3, $SrTiO_3$, WO_3, ZnO, and ZnS (Wu *et al.*, 2008). A major requirement resides in the chemical stability of such catalysts under light exposure. However, light irradiation involves energy consumption and increased operating costs that impede their large-scale implementation, unless using solar light. For these reasons, the design of new oxidative methods, more particularly ozone-based AOPs, turns out to be attractive.

2.3.3 The state of the art about ozonation

Under optimum operating conditions, ozonation and its improved variants appear to be the most promising routes for wastewater treatment, even those containing complex organic molecules such as antibiotics, estrogens and other drugs. Nowadays, a wide variety of mini- and micro-devices are available for domestic purposes, and more particularly for drinking water. Ozonation is progressively becoming an almost unavoidable technique for quick water purification, notwithstanding the low solubility of ozone in water, which barely reaches 570 $mg.L^{-1}$ at 20°C (Kumar and Sathyamurthy, 2013) for pure ozone in the gas phase. This solubility dramatically drops down at lower ozone concentrations in the gas phase according to Henry's law. Ozone can be conveniently generated through an electrical discharge using pure oxygen or even air, with an average energy consumption of 8-17 kWh per kg of ozone (Rice *et al.*, 1982, p. 255–285).

Molecular ozone is also fairly unstable in water with a half-life time ranging from few seconds up to few minutes, according to the pH of the liquid media. Between pH 7 and pH 10, the typical half-life time of ozone varies from 15 up to 25 min. The ozone reactivity arises from its two forms of resonance structures (Scheme 2.4), which explains the high probability of different type of chemical reactions such as cycloaddition, electrophilic and nucleophilic attacks.



Scheme 2.4. Ozone charge transition between two resonance structures

Ozone molecules exhibit a redox potential of 2.07 volts, which is supposed to induce sufficient reactivity to oxidize both organic and inorganic compounds (Kasprzyk-Hordern *et al.*, 2003):

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad (2.4)$$

In reaction 2.4, hydrogen does not undergo change in the oxidation state, unlike oxygen atoms which are reduced to (-2). In the meantime, the equilibrium potential of reaction 2.4 is switched to less positive values. The scavenging effect of protons partially impedes direct interaction of ozone with both the substrate and catalysts, and explains somehow why excessively acidic media are detrimental for ozonation processes. In less acidic media, the mere presence of hydroxyl anions turn out to be rather beneficial, inasmuch as direct ozone attack on hydroxyl anions generates highly reactive $^{\bullet}OH$ radicals (Reaction 2.5):

$$3O_3 + OH^- + H^+ \rightarrow 2\,{}^{\bullet}OH + 4O_2 \qquad (2.5)$$

$^{\bullet}OH$ radical displays a higher oxidation potential (2.33 V) (Kasprzyk-Hordern *et al.*, 2003), and a rate of attack typically 10^6 to 10^9 times faster as compared to molecular ozone (Munter, 2001). Increasing alkalinity in the reaction mixture should be beneficial, but beyond a certain threshold level, in metal cation-catalyzed ozonation the precipitation of catalytically active metal cations may take place. This indicates the occurrence of optimum pH. According to the mechanisms pathways proposed so far, molecular ozone behaves as a primary oxidant, and, once generated, the resulting $^{\bullet}OH$ radical act as secondary oxidizing agent (Park *et al.*, 2002). Unavoidably, $^{\bullet}OH$ can even react with ozone, thereby annihilating reciprocally their oxidizing capacities by generating much less reactive $HO_2^{\bullet}$ radicals (Reaction 2.6).

$$O_3 + {}^{\bullet}OH \rightarrow O_2 + HO_2^{\bullet} \quad (2.6)$$

$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + {}^{\bullet}OH \quad (2.7)$$

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^{\bullet} \quad (2.8)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (2.9)$$

The latter may also react with ozone into hydroxyl radical (Reaction 2.7), but at a lesser extent because of their relatively low reactivity. Since the concentration of ozone in aqueous media is limited by its low solubility, it clearly appears that excessive amount of hydroxyl radicals will enhance their detrimental scavenging effect on ozone molecules. Nonetheless, here care should be taken, because too alkaline pH's causes an increase in ozone decomposition into radicals with lower reactivity (Reaction 2.8). Some of these radicals ($2HO_2^{\bullet}$) may however behave as a valuable source for hydrogen peroxide (Reaction 2.9).

These findings constitute the base knowledge for improving the ozonation processes. In a first step, to overcome the major drawback related to low ozone solubility the contact time of ozone or the extent of the gas-liquid interface in the reaction mixture should be significantly increased. For this purpose a series of engineering solutions have been developed, e.g. high bubble dispersion and the use of long tubular reactors. In such devices, the overall reaction rate was found to depend on both the transfer rate of ozone from the gas bubbles to the liquid and the reaction rate of ozone with the organic pollutant (Canton *et al.*, 2003).

The low solubility of ozone in aqueous media has also stimulated research for developing chemical procedures, e.g. by using solid catalysts such as zeolites (Rubin, 2008). In this regard, fixed beds of porous glass or metal, or the use of solid catalysts that also act as adsorbents are also interesting routes to be explored. So far, free

transition metal ions and mixed oxides have shown interesting catalytic activity in the ozonation of organic pollutants (Shiraga *et al.*, 2006). However, catalyst loss and water contamination with metal cations are the main shortcomings in such methods. The use of supported metal cations is a possible solution in this regard, but the chemical stability of the solid support, more particularly in acidic media, should be an essential requirement for this purpose. In addition, metal cations should benefit of a certain mobility to be active, and ion-exchangers appear promising supports, but metal losses by leaching due to pH fluctuations are still possible. The frequency of the interactions occurring between ozone and the $^{\bullet}OH$ radicals may also be prevented by operating in laminar flow processes. Microfluidic processes in tubular reactors with internal coating showing catalytic activity in ozonation may constitute an interesting route to explore. Investigations should be focused in this direction.

Ozonation has seldom been applied for large scale purposes, more particularly in Europe, except in some special cases such as in the cleaning treatment of ship ballast water. This came as an alternative to negative impact of chemical compounds used for this purpose in conventional treatments (Goncalves and Gagnon, 2012). Here, total mineralization of refractory small molecules is an essential requirement to avoid natural water contamination. This can be achieved through powerful treatment methods such as catalytic ozonation and others (Ramirez *et al.*, 2010; Ping *et al.*, 2002).

When used in decolorizing textile wastewaters, conventional ozonation involves high ozone consumption. The latter is almost 4 times lower by catalytic ozonation (Yong *et al.*, 2005). In such purposes, ozone is usually injected at a concentration in the feed gas of 12.0 ± 0.5 mg L^{-1} and gas throughput of 1.0 L min^{-1} (Trapido *et al*,. 2005). In all possible applications, the electron density (ED) of the targeted molecules plays an

important role on the electrophilic attack of ozone. As a general feature, increasing ED accounts for increasing reactivity towards ozone.

This dependence may be significantly influenced by the presence of a catalyst (Fontanier *et al.*, 2005). For phenolic compounds, the reactivity towards ozone is strongly dependent on the number, type and position of functional groups attached to the aromatic ring, and generally decreases with decreasing number of hydroxyl groups. Methoxylated compounds were found to undergo lower total oxidation rates than phenolic derivatives (Mantzavinos, 2003).

Ozonation produces only partial degradation of pesticides in coupled chemical and biological treatments (Maldonado *et al.*, 2006). This often results in the formation of hazardous intermediates (Can and Gurol, 2003) For instance, when ozonated, phenolic compounds give rise to common derivatives such as resorcinol, catechol and hydroquinone, along with fumaric, maleic, glyoxylic, oxalic and formic acids (Beltran *et al.*, 2005). Such derivatives usually exhibit weak reactivity to oxidizing species, because of the presence of oxygen atoms in their structures (Gilbert, 2002). Antibiotics are typical organic pollutants in a wide variety of domestic and industrial wastewaters at sub-therapeutic concentrations. Seemingly, ozonation attempts at alkaline pH gave better performances than acidic media (Bin and Madej, 2012). Nonetheless, pH fluctuations during the ozonation process may produce changes in the mechanism pathways, making the elimination of the organic contaminant difficult to be monitored (Canton *et al.*, 2003; Azzouz *et al.*, 2010). Unless effective catalysts are used, drug and estrogen release in nature still remains a major issue to be addressed, as supported by an ample literature.

2.4 Catalytic ozonation

In surface catalysis, the overall rate of a physico-chemical process is governed by the contribution of different consecutive steps, and more particularly by the kinetic-controlling step (Fontanier *et al.*, 2005). Depending on the strength of the reagent-surface interaction, the ozonation process can involve physical or chemical adsorption. Too strong interaction of the reagents, intermediates or products leads to catalyst poisoning.

All ozonation methods involve heterogeneous processes, because it involves, at least, a surface reaction between a gas (ozone) and a liquid media containing the organic pollutant (Kasprzyk-Hordern *et al.*, 2003). The latter may be dissolved or merely dispersed as an emulsion (if liquid) or a suspension (if solid). That is why care should be taken when using abusively the terms ''homogenous catalytic ozonation'' (Kasprzyk-Hordern *et al.*, 2003). The latter arise from an incorrect denotation that should be avoided as much as possible, whatever the catalyst physical state may be.

The first catalyst ever used in preliminary ozonation studies were dissolved metal cations. Up today, salt of transition metals such as Fe^{2+}, Fe^{3+}, Mo^{6+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ag^{+}, Cr^{3+}, Zn^{2+} are still used as catalysts for this purpose (Legube and Karpel Vel Leitner, 1999; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014; Liotta *et al.*, 2009). Bivalent cations and more particularly Fe^{2+} ions showed so far the higher catalytic performances (Azzouz *et al.*, 2010; Liotta *et al.*, 2009). In Fenton process, Fe^{3+} cation is assumed to decompose H_2O_2 into oxygen and water without generating the targeted hydroxyl radicals (Elhamshary *et al.*, 2011). In the ozonation process, a key step resides in the direct interaction between ozone and bivalent iron cations (Reaction 2.10). This reaction is supposed to take place, giving rise to FeO^{2+} cation.

The latter is now recognized as being the main precursors of hydroxyl radical even in acidic media (Reaction 2.11).

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (2.10)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (2.11)$$

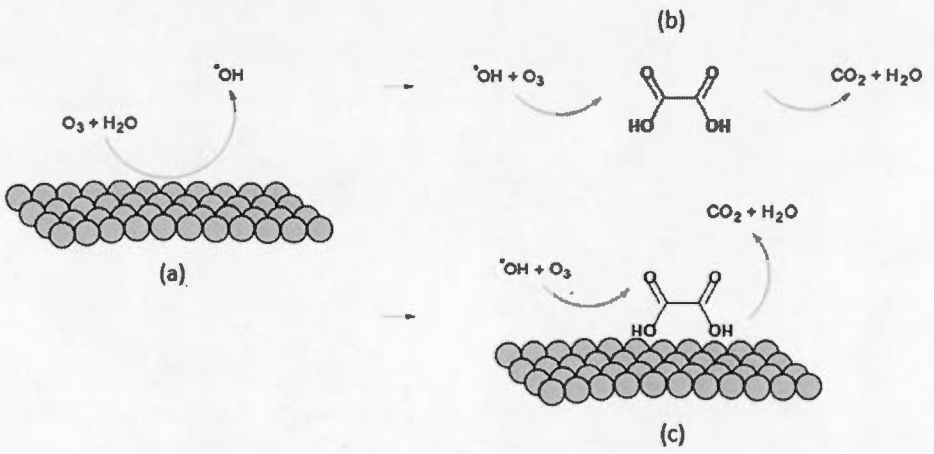
The formation of OH^- anions induces unavoidably a pH increase and changes in the mechanism pathways (Canton *et al.*, 2003; Azzouz *et al.*, 2010). This is expected to cause catalyst loss through metal cation precipitation, and to shift equilibrium towards an attenuation of reaction 2.11. This is a major drawback that makes the implementation of large scale cation-catalyzed ozonation difficult to be achieved. Besides, the presence of metal cations in the treated wastewaters is another major issue to be addressed, and the use of insoluble solid catalyst appears as a more promising alternative. Oxide of metals such as Cu, Mn, Co, Cr, V, Ti, Bi, and Zn in different oxidation states and supported or free metal particles such as Ir, Pd, Pt, Rh, and Ru can be used for this purpose.

The use of solid or supported catalysts aims not only to overcome these shortcomings, but also to provide extended specific surface are for improving the contribution of adsorption (Wu *et al.*, 2008; Canton *et al.*, 2003). The latter will be more or less significant according to acid-base properties of the solid surface. So far, a wide variety of solid supports have been tested in ozonation attempts.

Granular Activated Carbon (GAC) can be used as support for metal oxide immobilization. In spite of a series of drawbacks (fast saturation and need to regeneration or replacement and low efficiency on COD removal), GAC-catalyzed ozonation involves low ozone consumption, owing the high specific surface area of the solid support and its high capacity to generate hydroxyl radicals in the aqueous phase (Ping *et al.*, 2002).

In the presence of solid catalysts, ozonation is assumed to take place not only in the bulk solution, but also on all the interfaces involved between the different phases present in the reaction mixture (Guo *et al.*, 2012; Legube and Karpel Vel Leitner, 1999). Ozonation on the catalyst surface should prevail, as supported by the significant enhancement as compared to the non-catalyzed process. In this case, the adsorption of at least one reagent turns out to be an essential requirement for the surface reaction and the formation of $^{\bullet}OH$ radicals.

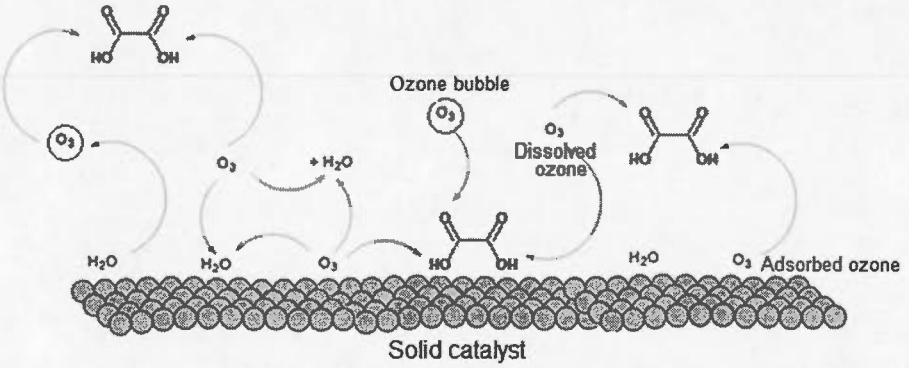
The ozonation of oxalic acid is an interesting example of oxidative decomposition of refractory organic compound. In this case, a first postulated mechanism is the one involving simultaneously all species adsorbed on the catalyst surface (Scheme 2.5a→c). The second reaction pathway (Scheme 2.5a→b) proposes a previous dissolution of ozone in the aqueous solution followed by its adsorption from the liquid media onto the solid surface. This is supposed to enrich the catalyst surface with oxidizing species. The consecutive adsorption of the organic molecules will produce their decomposition and possibly the catalyst regeneration by reduction.



Scheme 2.5. Interfacial radical generation (a) and radical action on oxalic acid in the bulk solution (b) and on the catalyst surface (c).

Once desorbed, the products of this step will be oxidized by $^{\bullet}OH$ in the bulk solution. In both types of mechanisms, chemisorption of at least one of the reagents is essential, but simultaneous adsorption of two or more substrates should be more beneficial for the ozonation process. The global ozonation process may simultaneously involve both mechanisms and probably other reaction pathways involving diverse adsorbed-adsorbed, adsorbed-dispersed and dispersed-dispersed species interactions.

The preponderance of each type of interaction must be strongly dependent on the affinity of the catalyst surface towards a given species, and may vary according to the operating conditions and chemical composition of the reaction mixture. This implies that various interactions between all types of ozone present in the reaction mixture (dispersed gas bubbles, dissolved and adsorbed) with the organic substrates in their adsorbed and (or) soluble forms, along with dispersed hydrophobic clusters (if insoluble) are possible (Sui *et al.*, 2011). The high complexity of such a heterogeneous catalytic process is illustrated merely by the high number of direct interactions involving the primary chemical species, i.e. ozone and oxalic acid in the vicinity of a solid surface (Scheme 2.6).



Scheme 2.6. Possible direct interactions between the primary ozone species with adsorbed and unadsorbed oxalic acid in the vicinity of a catalyst surface

This explains why kinetic study of ozonation in the presence of solid catalysts still remains a challenge to be considered. Here, the affinity of the catalyst surface towards ozone, water and (or) the organic substrate is expected to determine the kinetic-controlling step, once the issues related to the low solubility of ozone and the hydrophobic character of the organic substrate in the aqueous media are addressed. The type of solid catalyst must be a key factor when applying ozonation in the decomposition of specific organic molecules.

2.5 Solid catalysts for ozonation

A wide variety of catalysts have been tested in heterogeneous oxidative processes, as reported by an ample literature succinctly illustrated by some attempts summarized in Table 2.1. A special attention has been focused on dispersed or supported metal oxides, more particularly of titanium, carbon-based materials, zeolites and certain microporous aluminosilicates. Among these, clays minerals are the most abundant in nature, and appear as promising catalysts for such purposes.

Table 2.1. Solid catalysts for oxidation processes

Catalyst	Organic compound	Oxidation conditions	Cat (gL^{-1})	Init pH	Time (min)	T (^0C)	Yield (%)	Ref.
Modified ceramic honeycomb	Nitrobenzene ($50\mu gL^{-1}$)	C_{ozone} =1.0 mg L^{-1}	-	6.92	-	25	80	(Zhao *et al.*, 2009)
Mn^{2+} (dispersed) MnO_2	C.I. reactive red 2 (100 mg L^{-1})	Ozone: 200 mL min^{-1}	0.1 0.8	2.0	-	25	99	(Wu *et al.*, 2008)
Fe-laponite	Phenol (10^{-3} M)	C_{H2O2}=0.05 M	1.0	3.0	-	30	100	(Ramirez *et al.*, 2010)
Granulated carbon, Carbon black, graphite	Phenol (5 g L^{-1})	Oxidation by air	1.0	-	60	20	100	(Stuber *et al.*, 2005)
hydrotalcite	Phenol (10^{-3} M)	Ozone: 200 ml h^{-1}	1.0	-	-	20	100	(Shiraga *et al.*, 2006)
MnO_2 ,Cr_2O_3 ,TiO_2 , Al_2O_3 ,Ni_2O_3 , CuO, MoO_3,CoO ,Fe_2O_3	m-dinitrobenzene (10^{-3} M)	Ozone: 1.0 L min^{-1}	1.0	3.0	120	20	80-100	(Trapido *et al*,. 2005)
Fe^{3+} exchanged zeolite	Phenol (0.069 M)	C_{H2O2}= 0.1 M	0.35	2.5	180	70	77	(Liotta *et al.*, 2009)
Polyamidoxime complexes with Cu, Zn, and Fe	Phenol (10^{-3} M)	C_{H2O2}= 10^{-2} M	4.0	9.0	240	25	92, 85, and 87 respect.	(Elhamshary *et al.*, 2011)
MnOx/MCM-41	Nitrobenzene (120 $\mu g.L^{-1}$)	Ozone: 400 mL min^{-1}	1.0	6.91	-	15	90	(Sui *et al.*, 2011)
Mn-Ce-O	Phenolics in olive mill wastewater	Mn/Ce ratio : 70/30 Ozone : 500 ml min^{-1}	10	3.4	120	25	91	(Martins and Quinta-Ferreira, 2009)

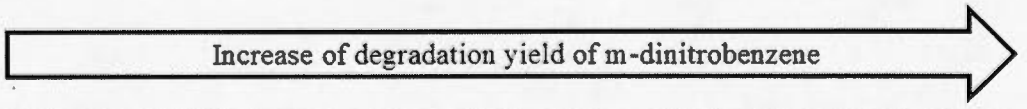
MnO_2	oxalic acid (10^{-3} M)	Ozone: 150 ml min^{-1}	0.5	3.0	45	-	99	(Orge *et al.*, 2012)
Nano structured cerium oxide	Oxalic acid (10^{-3} M)	C_{ozone}=50 g m^{-3} Ozone:150 ml min^{-1}	0.15	3.0	180	25	75	(Orge *et al.*, 2011)
Nano structured cerium oxide	Aniline (10^{-3} M)	C_{ozone}=50 g m^{-3} Ozone: 150 ml min^{-1}	0.15	6.0	30	25	100	(Orge *et al.*, 2011)
Goethite	Phenanthrene (25 ppm)	C_{H2O2}= 5 M	3.3	7.0	720	-	70	(Orge *et al.*, 2011)
ZnO nanocrystals	Diazinon (20 mg L^{-1})	UV lamp 30 W-253.7 nm	0.15	6.5	80	-	80	(Daneshvar *et al.*, 2008)
ZnO nanocrystals	Phenol (100 mg L^{-1})	Ozone: 0.55 mg min^{-1}	1.25	-	60	25	90	(Dong, *et al.*, 2011)
Carbon nanotube supported MnO_2	Ciprofloxacin (30.2 µM)	Ozone: 400 mL.min^{-1} C_{ozone} =0.40 mg min^{-1}	1.0	7.0	15	20	89	(Sui *et al.*, 2012)
TiO_2/Al_2O_3 Ratio: 1/9 wt.%	Dimethylphthalate (0.4 mM)	Ozone: 1.95 L min^{-1}	10	5.6	30	-	100	(Chen *et al.*, 2011)
Co and Mn doped γ-Fe_2O_3	2,4-dichlorophenoxyacetic acid (20 mg L^{-1})	C_{ozone}=30 mg L^{-1} Ozone: 12 L h^{-1} Fe^{3+}/Co^{2+} mole ratio=2	0.8	6.0	-	20	99	(Lv *et al.*, 2010)
Fe_2O_3/CeO_2 on activated carbon	Sulfamethoxazole (100 mg L^{-1})	C_{ozone}=48 mg L^{-1} Ozone : 1 L min^{-1}	2.0	3.0	-	25	100	(Akhtar *et al.*, 2011)
Nickel supported activated carbon	p-chlorobenzoic acid (10 mg L^{-1})	Ozone: 50 mg h^{-1}	5.0	4.31	60	25	100	(Li et *al.*, 2009)
Activated carbon supported cerium	dimethyl phthalate (30 mg L^{-1})	Ozone: 50 mg h^{-1} Ce amount: 1% w/w	0.5	5.0	60	25	100	(Orge *et al.*, 2011)
Cerium oxide	Oxalic acid (10^{-3} M)	C_{ozone}= 50 g m^{-3} Ozone: 150 ml L^{-1}	0.5	3.0	180	25	85	(Goncalves, 2012)

MWCNT	Oxalic acid ($2.5x10^{-4}$ M)	Ozone: 480 mL.min^{-1} C_{ozone} =20 mg min^{-1}	0.1	3.0	40	20	80	(Liu *et al.*, 2011)
Fe/SBA-15	Dimethylphthalate (10 mg L^{-1})	C_{ozone}=50 mg h^{-1} Ozone: 0.8 L min^{-}	0.2	5.7	60	25	100	(Huang *et al.*, 2011)
Fe/MCM-41 0.5% w/w Fe	p-chlorobenzoic acid (10 mg L^{-1})	Ozone: 1.2 L min^{-1} C_{ozone}=100 mg h^{-1}	1.0	4.3	20	25	100	(Huang *et al.*, 2012)
Co-Mn-Al	Nitrobenzene (10^{-5} M)	C_{ozone}=0.41 mg min^{-1} Ozone: 400 ml min^{-1} Co/Mn/Al ratio: 4/2.13/0	0.5	6.99	10	19	60	(Sui *et al.*, 2012)

Comparison between specific performances of specific pollutant-catalyst-oxidizing agent systems is quite difficult, and is not targeted in the present work, because of specific operating conditions. However, a deep analysis of the data of Table 2.1 may be useful to understand the essential requirements for a catalyst to achieve total mineralization of any organic molecules, which remains the main objective of this chapter.

2.5.1 Metal oxides and metals

MnO_2, TiO_2, Al_2O_3, Fe_2O_3, WO_3, CuO, CeO_2, Ni_2O_3, CoO, V_2O_5, Cr_2O_3, MoO_3, CeO, and CuO-CeO_2 mixtures represent typical examples of metal oxide catalysts that may exhibit different activities in ozonation processes according to the organic substrate to be oxidized. For instance, Al_2O_3 and MnO_2 were found to produce different decomposition yields with 2-chlorophenol and oxalic acid (Stuber *et al.*, 2005; Matheswaran *et al.*, 2007). Conversely, for a given organic substrate such as *m*-dinitrobenzene, extensive studies (Trapido *et al*,. 2005; Nawrocki and Kasprzyk-Hordern, 2010) have shown that the catalyst activity in ozonation varies according to the type of the metal oxide used, in the following sequence (Scheme 2.7).



ozone alone≈MnO_2 ≈Cr_2O_3 <TiO_2 <Al_2O_3 <Ni_2O_3 ≈ CuO < MoO_3<CoO <Fe_2O_3

Scheme 2.7. Variation of the catalytic activity versus the metal oxide in the degradation of *m*-dinitrobenzene

TiO_2 is a conventional and low cost catalyst widely used in photo-oxidative processes (Gilbert, 2002), but a growing interest is now focused on new photoactive catalysts such as CdS, ZnS, α-Fe_2O_3 (Shivaraju, 2011; Tizaoui *et al.*, 2008, Singh *et al.*, 2011; Chen *et al.*, 2009). Several transition metal oxides and their mixtures such as Mn-Ce-O showed catalytic activity in the ozonation of phenols (Liotta *et al.*, 2009; Martins and Quinta- Ferreira, 2009). When separated, unlike cerium oxide, manganese oxide produced a complete degradation of oxalic acid after 45 minutes of ozonation, and showed a constant catalytic activity even after three cycles of oxidation (Orge *et al.*, 2012).

These differences in catalytic activity can be partly explained by the specific features of the catalyst surface, more particularly the acid-base properties of each catalyst, which must play a key-role in the adsorption of the reagents. For instance, moderately acidic surfaces such as clay-supported metal cations were found to produce appreciable degradation yields of oxalic acid due to a synergy between adsorption and the catalytic activity of the exchangeable cations (Azzouz *et al.*, 2010). The latter may act on the catalyst surface and (or) in the bulk solution, according to its mobility in the vicinity of the catalyst surface, which strongly depends on the pH level of the reaction mixture. Similar synergy was also noticed for nano-structured cerium oxide catalysts (Orge *et al.*, 2011).

Effective adsorption supposes high specific surface area, which usually requires increased porosity and (or) high catalyst amount. However, high ozonation levels require optimum catalyst quantities in correlation with adequate pH levels, as supported by the complete mineralization of phenanthrene on goethite at pH 7.2 (Park *et al.*, 2002; Kanel *et al.*, 2003), of oxalic acid on iron-exchanged montmorillonite at pH 3.0-3.5 (Azzouz *et al.*, 2010) or of the diazinon insecticide on ZnO nanocrystals at pH 5.2.

Under similar operating conditions, the catalyst characteristics play a key-role even in the case of almost similar structures. For instance, ZnO nanoparticles showed higher efficiency in phenol ozonation, as compared to manganese and cerium mixed oxides (Daneshvar *et al.*, 2008; Dong, *et al.*, 2011). This was partly explained in terms of higher surface area, the other contribution being attributed to the metal characteristics. The dispersion state of metal oxides does not seem to play a significant role, inasmuch as both dispersed manganese oxide and carbon-supported manganese oxides showed high catalytic activities at acidic pH, which is supposed to involve mainly the action of molecular ozone (Sui *et al.*, 2012). In some ozonation processes, metals appear to exhibit higher catalytic activity in their cationic form, as supported by the higher ozonation efficiency in the presence of Mn^{2+} as compared to MnO_2, more particularly at pH 2 (Wu *et al.*, 2008). This was also explained by the involvement of molecular ozone attack, presumably due to an enhancement of the direct interaction with more mobile and available cations in acidic media as a result of partial metal oxide dissolution in acid media.

This explains that, notwithstanding its apparently lower effectiveness, MnO_2 is still tested in the ozonation in controlled acidic media of a wide variety of organic substrates such as oxalic acid, pyruvic acid, sulfosalicylic acid, propionic acid, glyoxalic acid, and phenol. TiO_2-supported MnO_2, FeOOH and SnO_2, brucite and magnesia, magnetic cobalt and Mn-doped γ-Fe_2O_3, granular activated carbon have also been tested as catalysts in ozonation processes (Chen *et al.*, 2011; Lv *et al.*, 2010; Gul *et al.*, 2007). The growing interest devoted to metal oxides resides, thus, in their ability to act as cation sources in moderately acidic pH through partial dissolution. Nevertheless, even though metal cations are supposed to act as the main catalytic species, many aspects related to their mechanism pathways still remain to be elucidated.

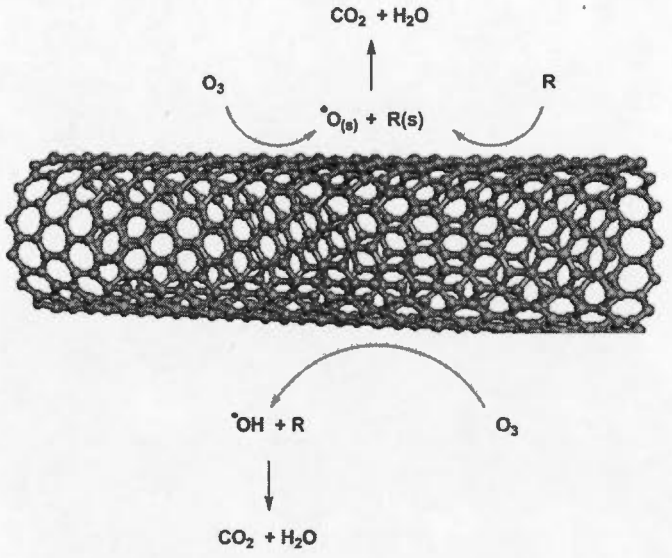
Solids may also be used as supports for catalysts. In this regard, except organic solids such as polymers and dendrimers, which are known to be highly reactive towards ozone, all kinds of materials that exhibit sufficiently high stability against irreversible oxidative decomposition can be used as catalyst supports. So far, a wide variety of inorganic supports such as zeolites, clay minerals, silica gel, Al_2O_3 or TiO_2 have been used for this purpose (Legube and Karpel Vel Leitner, 1999). Zeolite and alumina showed the lowest catalytic activities (Legube and Karpel Vel Leitner, 1999; Neitner *et al.*, 1999; Lin *et al.*, 2000). For instance, TiO_2/ $Fe^{2+}$and TiO_2/ Fe^{3+} turned out to be interesting catalysts for the oxidative decomposition of many organic pollutants. Alumina-supported TiO_2 or Fe_2O_3 have been employed for removing oxalic acid, chloroethanol and chlorophenol from water (Cooper and Burch, 1999), or fulvic acid from wastewater (Volk *et al.*, 1997). Ruthenium and cerium oxides have been tested for succinic acid removal (Legube and Karpel Vel Leitner, 1999). Reportedly, supported noble metals such as Pt/TiO_2 and Pt/Al_2O_3 can produce total decomposition of organic compounds (Liotta *et al.*, 2009). Ru/CeO_2 systems appear to produce complete removal of succinic acid from wastewater after only 60 minutes (Leitner *et al.*, 2000) taking into account that total decomposition of most organic contaminants still remains a difficult challenge to achieve.

2.5.2 Carbon-based catalysts

These last years, many types of carbon based structures have been tested as catalysts or supports in oxidative processes, and have produced more or less satisfactory results in the decomposition of a wide variety of organic molecules. Indeed, GAC, carbon black powder and graphite have been employed as catalysts or catalyst supports for Pt, Pd, Ru in the oxidation of phenols and halogenated phenols, carboxylic acids such as acrylic, acetic, formic, oxalic, succinic, adipic, propionic,

glutaric, and butyric acid (Stuber *et al.*, 2005). Fe_2O_3 and CeO_2 immobilized on activated carbon turned out to be effective catalysts in the ozonation of antibiotics (Akhtar *et al.*, 2011). Activated carbon-supported nickel showed significant catalytic activity in the ozonation of *p*-chlorobenzoic acid as compared to non-catalytic processes (Li et *al.*, 2009).

Ozone-Granulated Activated Carbon (O_3/GAC) is a typical example of catalytic ozonation, which produces intense degradation of pesticides (Munter, 2001; Trapido *et al*,. 2005). In the oxidation of oxalic acid, cerium oxide showed lower activity than its carbon-supported counterpart (Orge *et al.*, 2011). Here, the specific surface area and metal oxide particle diameter are supposed to play key roles (Goncalves *et al.*, 2012). Another interesting carbon-based structure is the so-called Multiwalled Carbon Nano Tubes (MWCNTs), which consists in mesoporous nanomaterials with linear channels. Reportedly, oxidation attempts using such materials resulted in exhaustive phenol decomposition (Liotta *et al.*, 2009), with interesting behavior towards refractory intermediates such as oxalic acid (Liu *et al.*, 2011). As many types of solid catalysts, MWCNTs appear to act as initiators for surface bound oxidative species (Scheme 2.8).



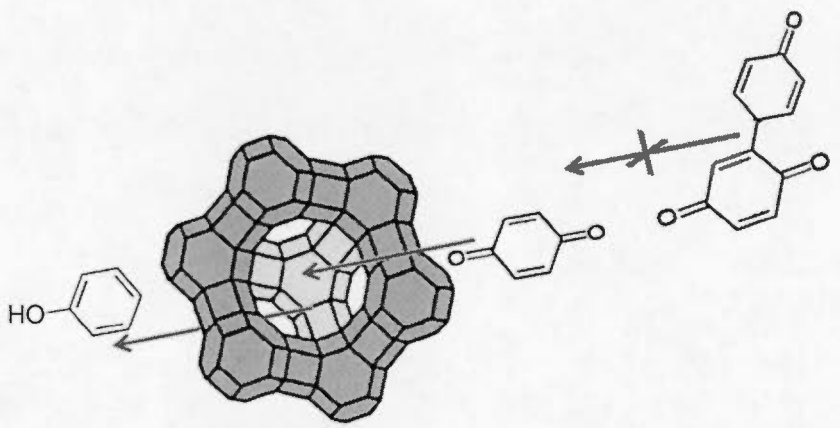
Scheme 2.8. Schematic representation of possible interactions for oxalic acid ozonation on MWCNTs

On such materials, oxidation of organic molecules was found to take place not only in the bulk solution but at the catalyst surface as well (Nawrocki and Kasprzyk-Hordern, 2010). The general tendency is that, the use of solid catalysts is beneficial, because the global oxidation process often involves a complementary contribution of the surface adsorption steps. Such enhanced oxidation processes may lead to complete mineralization of the organic molecules. This implies that the extent of the specific surface areas should play a key role as in any solid-fluid interface processes, and that expanded structures having high surface-to-bulk ratio should be strongly recommended catalysts or catalyst supports for this purpose. Aluminosilicates such as zeolites, clays and clay minerals must be very interesting in this regard.

2.5.3 Zeolites and related catalysts

Aluminosilicate family includes a wide variety of amorphous and crystalline phylosilicates such as clays and clay minerals, and tectosilicates such as zeolites. The common feature of all these structures resides in the occurrence of permanent negative charges arising from the replacement of $[SiO_4]$ tetrahedra by $[AlO_4]^-$ anions. These charges can be compensated by cations usually belonging to alkali and alkaline earth metals. Aluminosilicates are solid acids, which have been used as catalysts in many chemical processes.

Zeolites are crystalline and microporous aluminosilicates that can offer high specific surface area for adsorption and catalysis. Such structures have 3-D frameworks with channels and cavities that can allow diffusion of a wide variety of organic molecules with critical diameter around that of monoaromatic hydrocarbons, such as benzene, toluene, xylene and other monoaromatic derivatives (Scheme 2.9).



Scheme 2.9. Molecular sieving property of zeolites. Here, as an example, phenol and p-benzoquinone can diffuse freely across the zeolite channels and cavities, unlike bulkier molecules

They have already been tested as catalysts in the ozonation of organic molecules. Seemingly, this oxidation reaction is related to ozone interaction with Lewis acid on the zeolite surface, and an increase in surface acidity through suitable modification enhances the process efficiency (Valdesa *et al.*, 2009). Ferric ion is well known to exhibit a special capacity for decomposing organic molecules in the presence of oxidizing agent, and an ample literature is available in this regard. Fe^{2+} ion exchanged zeolites were also found to display the highest effectiveness, by achieving almost total removal of organic pollutants from certain wastewaters (Liotta *et al.*, 2009).

Pseudo-zeolites are similar to zeolites by their crystalline 3-D frameworks build with cavities and interconnected channels, but are not aluminosilicates like zeolites. Mesoporous silicas like MCM and SBA series are regarded as being pseudo-zeolites. Some of these materials such as MCM-41 produced appreciable toluene removal yield of up to 96% from contaminated wastewaters (Kwong *et al.*, 2008). The general tendency is that MCM-41 showed higher effectiveness in ozonation attempts as compared to zeolites, most likely due to their higher specific surface area (975 $m^2.g^{-1}$ versus 530 $m^2.g^{-1}$).

Reportedly, mesoporous Fe^{3+}/SBA-15 silica produced total decomposition of dimethylphhtalate through ozonation at pH 5.7. However, such a performance account for only 35% removal yield of total organic compounds (TOC), providing clear evidence that no thorough mineralization into CO_2 took place. Raising pH up to 9.0 was found to produce a slight enhancement in TOC removal, suggesting an $^{\bullet}OH$ radical mechanism. This is supported by the detrimental effect produced by the addition of an $^{\bullet}OH$ radical scavengers (Liu *et al.*, 2011). On such materials, excessive amounts of cations and anions seem to affect the overall SBA-15 activity (Huang *et al.*, 2011). Fe/MCM-41 showed appreciable catalytic activity in the ozonation of *p*-

chlorobenzoic acid in aqueous media, affording TOC removal yields of more than 94.5% after 60 minutes of oxidation. Under similar conditions, the TOC removal yields were only 61.5% on MCM-41 and 62.3% without catalyst. Here also, such a process seems to occur via $^{\bullet}OH$ mechanism pathway. Seemingly, the catalyst effectiveness is maximum for an optimum iron amount of 0.5% (Huang *et al.*, 2012). Similar phenomenon was observed on MnO_2 supported on mesoporous silica (MnO_2/MCM-41). Such catalysts produced a nitrobenzene oxidation yield of up to 93.3% after 10 minutes of ozonation in the presence of an optimum MnO_2 amount of 1.15% (Sui *et al.*, 2011).

2.5.4 Mixed hydroxide catalysts

Layered double hydroxides (LDH) are anionic clay minerals, which have also been used as ozonation catalysts. In this regard, Co-Mn-Al –LDH in different Co/Mn amount ratio have been tested in the ozonation of nitrobenzene, Co_4Mn_2-Al-LDH sample was found to produce the highest degradation yield of 60% at pH 6.99 and room temperature (Sui *et al.*, 2012). Interestingly, the yield of mineralization into CO_2 did not exceed 20% with the same catalyst under similar conditions, indicating the formation of large amount of intermediates. This appears to be a common feature of many LDH-based catalyst, and a possible explanation is the surface basicity that might not favor adsorption like in acidic media. As a confirmation in this regard, deeper insights showed that increasing cobalt amounts enhance the catalytic activity.

In contrast, increasing Al amounts were found to be detrimental, presumably due to an enhancement of the surface basicity (Azzouz *et al.*, 2010). Reportedly, hydrotalcite, which consists in an Al-Mg-LDH material, has been tested in phenol oxidation (Liotta *et al.*, 2009), but, seemingly, higher performance in the catalytic

ozonation of phenol and oxalic acid in water was registered when used as a support for metal oxides such as CuO (Shiraga *et al.*, 2006). Total disappearance of phenol was measured after less than 30 minutes and total mineralization of oxalic acid was obtained upon 210 minutes of catalytic ozonation. Such a performance still remains, by far, below those registered with cationic clay minerals. Performance comparison is difficult, because different catalyst-pollutant systems require different operating conditions, but may be useful for understanding the main approaches in this research area.

Ferral is natural material composed of aluminum sulfate, ferric sulfate, ferric oxide, aluminum oxide, and magnesium oxide. Reportedly, high decomposition yields of organic dyes of up to 99% were obtained through wastewater ozonation at acidic pH (Hassana and Hawkyard, 2002). Here, the mere presence of Fe cations, most likely due to partial dissolution of the material, seems to play a key role in the catalytic activity of such material. Thus, it clearly appears that free metal cations in the vicinity of a solid surface is an essential requirement for enhancing interaction with all the ozone forms present in the reaction mixture.

Among the wide variety of solid catalysts tested so far, only aluminosilicates, and more particularly clay minerals, appear to fulfill this requirement that favors cation mobility and catalytic activity. Interesting and low cost aluminosilicates are those belonging to the smectite clay mineral family, more specifically montmorillonite, the main component of bentonites. A special interest is now devoted to this clay mineral due to its high surface area of up 200 $m^2.g^{-1}$ and even beyond through suitable modification procedures, increased cation exchange capacity, high adsorption and swelling capacity, as compared to other counterparts.

2.5.5 Clays, clay minerals and montmorillonite

Unlike zeolites, clay minerals are dispersed crystalline frameworks, most of them having layered structures but almost similar surface properties as zeolites. Their wide abundance in nature makes them to be regarded as low cost alternatives to zeolites in many applications. There exist various types of clays, which are natural raw mixtures of clay minerals, volcanic ashes, silicas, carbonates and miscellaneous. One of the most representative clays is bentonite and one of the most studied clay mineral is montmorillonite (Bergaya *et al.*, 2006). Bentonite is a clay material mainly composed by smectite and other minerals like feldspar, biotite, quartz, pyroxenes, and zircon (Murray, 2007, p. 161–178). Smectite is a family of several minerals such as montmorillonite, saponite, vermiculite, nontronite, hectorite, volkonskoite, sauconite, and beidellite. Kaolinite is also another clay family that differs from smectites by the layer number and arrangements.

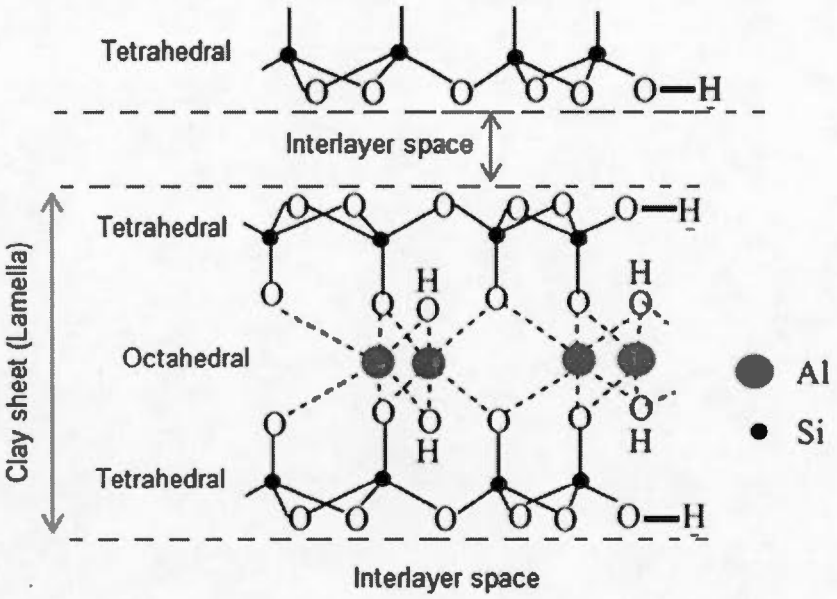
Many examples of clay-catalyzed oxidation processes at room temperature have been reported in the literature. Al-Fe pillared clays (Al-Fe PILCs) were found to display improved catalytic activity in phenol oxidation at moderately acidic pH values (Ramirez *et al.*, 2010; Barrault *et al.*, 2000). Cu-doped alumina-pillared montmorillonite have been successfully used for oxidation of toluene and xylenes (Wu *et al.*, 2008; Bahranowski *et al.*, 1999). Phenol oxidation has also tested on metal-exchanged clays and pillared clays (Liotta *et al.*, 2009). (Al-Fe)-PILC showed the highest performance, affording removal yields of up to 100%.

Attapulgite-based catalysts were reported to improve by about 20% the TOC removal as compared to the non-catalytic ozonation (Legube and Karpel Vel Leitner, 1999). Reportedly, Fe doped laponite produced total removal of phenolic compounds,

antibiotics and azo-dyes from wastewaters (Ramirez *et al.*, 2010). Ceramic honeycomb modified by impregnation of metals such as Mn, Cu gave conversion yield of about 80% in the ozonation of aqueous solutions of nitrobenzene. This conversion yield is three times higher than that of non-catalytic ozonation (Zhao *et al.*, 2009).

Montmorillonite is probably one of the most studied clay mineral (Bergaya *et al.*, 2006), whose surface properties can be significantly improved through simple procedures, providing effective materials for adsorption and catalysis (Nagendrappa, 2002; Kaur and Kishore, 2012), more particularly in oxidation reactions (Lei *et al.*, 2007; Pillai and Demessie, 2003; Jagtap and Ramaswamy, 2006). The structure of each montmorillonite sheet consists of a layer of octahedral alumina $[Al_2(OH)_6]$ sandwiched between two layers of tetrahedral silicates $[SiO_4]^{4-}$ (Scheme 2.10).

In the presence of water molecules, the interlayer spacing enlarge, inducing clay swelling that facilitates exchange of the interlayer cations, usually Na^+, Ca^{2+} and Mg^{2+}. The surface negative charges originate from isomorphous substitution of Al^{3+} by Mg^{2+} species in the structure of the octahedral layer. In dry montmorillonite, the exchangeable cations are located within the hexagonal cavities of the silica layer, but upon hydration, the cations move into the interlayer spacing (Nagendrappa, 2002).



Scheme 2.10. Structure of montmorillonite

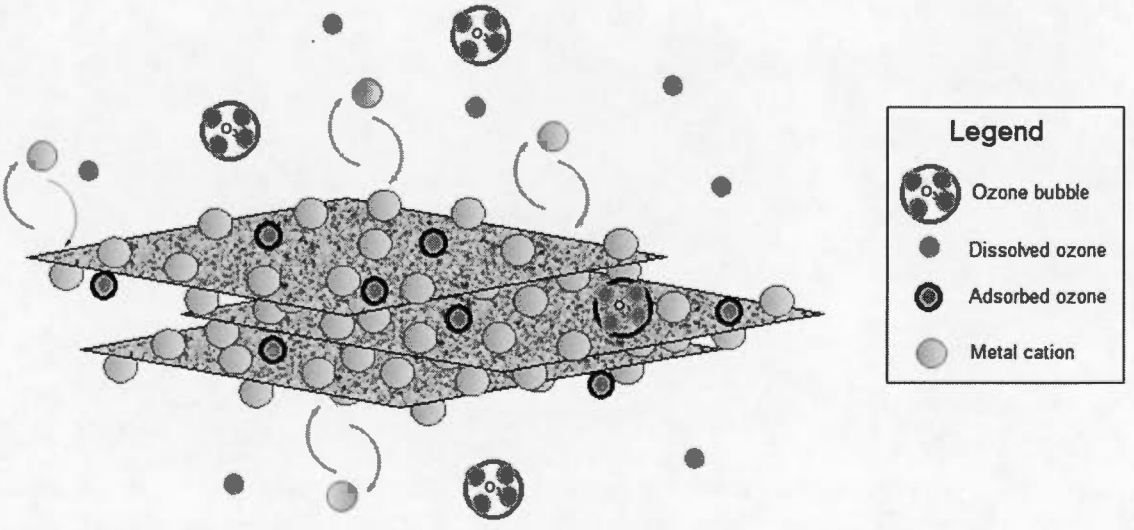
The strength distribution of these acid sites can be modified by ion-exchange, dealumination through acid attack or incorporation of alien molecules or particles. Incorporation of heavier metal cations displaying high solvation capacity is known to generate Brønsted and Lewis acid sites. The Brønsted acidity originates from the dissociation of the intercalated water molecules coordinated to cations, as illustrated by reaction (2.12):

$$[\text{Metal}(H_2O)_n]^{3+} \rightleftharpoons [\text{Metal}(H_2O)_{n-1}OH]^{2+} + H^+ \qquad (2.12)$$

Heating up to 200-300°C is known to induce a decrease in the Brønsted acidity but an increase in Lewis acidity. Excessive heating to around 450°C and above usually results in complete dehydroxylation of the aluminosilicate lattice and a thorough conversion of Brønsted acid sites into Lewis acidity.

An additional feature of montmorillonite resides in its double-faced lamella structure. The latter offers twice its capacity to retain both adsorbed and dispersed metal cations in the vicinity of the solid surface. Moderately acidic pH are already found to favor weak ion-exchange by proton, providing, thereby, sufficient released cation that can also have interaction with unadsorbed molecules of ozone and organic substrate (Azzouz, 2012; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014). Besides, both faces of montmorillonite lamellae possess sufficient electrostatic charges that improve the adsorption capacity. The solid surface can attract and concentrate not only the organic substrate molecules, but also ozone in both adsorbed and dissolved forms, along with dispersed micro-bubbles (Scheme 2.11).

High catalytic activity requires high number of available clay sheets devoid of dense silica phases that do not contribute to the above mentioned surface processes. In some cases, clay mineral purification turns out to be necessary for ozonation processes because of the presence of carbonates, bicarbonates and organic materials may affect



Scheme 2.11. Metal cation mobility and ozone concentration in the vicinity of homo-ionic form of montmorillonite surface.

ozone efficiency. In oxidative processes, carbonates and bicarbonates are known to act as radical scavengers, while organic components involve undesired competitive ozonation processes. Convenient and effective purification of montmorillonite involves full ion-exchange into the desired homoionic form, combined with a selective sedimentation in water under ultrasound exposure and removal of the lower fraction that contains various ashes, dense phases like quartz, and other impurities. Purification may be completed by either ozone bubbling at room temperature or controlled calcination up to 400-450°C to remove possible carbonates and (or) organic impurities. The final step involves dialysis in water in order to remove the excess salt resulting from ion-exchange (Bergaya *et al.*, 2006). In most cases, montmorillonite-based catalysts are prepared starting from the Na^+ exchanged (NaMt) (Bergaya *et al.*, 2006; Joshia *et al.*, 2009; Lin *et al.*, 2002; Boufatita *et al.*, 2008). All these purification steps do not use organic solvent, and are fairly easy to carry out in water at ambient temperature and pressure.

2.6 Key parameters in catalytic oxidative processes

2.6.1 Catalyst amount and lifetime

Ozone appears as being the most convenient oxidizing agent in terms of production, handling and consumption constraints, as supported by an ample literature in this regard. Indeed, even in the absence of catalyst, cost comparison showed that ozonation is much more effective in terms of reaction time than photochemical and Fenton oxidative processes or even than adsorption on granulated active carbon in dimethylphenol elimination (Munter *et al.*, 2006). Under similar common conditions, the required time for total decomposition of dimethylphenol, by Fenton process was 35 minutes while the same process could be achieved through ozonation in only 13

minutes in acidic medium and 7 minutes in alkaline medium. The required amount of oxidizing species (H_2O_2) in Fenton process is 680 mg L^{-1}, while ozone doses of only 13 and 25 mg.L^{-1} are needed in alkaline and acidic media, respectively (Munter *et al.*, 2006). In all cases, the use of optimum catalyst concentrations was found to modify favorable the reaction mechanisms towards an improvement of the process efficiency (Yong *et al.*, 2005), and an increase of the quantities of the oxidizing agents (Yong *et al.*, 2005; Elhamshary *et al.*, 2011; Piera, *et al.*, 2000; Chedeville *et al.*, 2005).

This allows envisaging large-scale facility implementations, notwithstanding that research is still in progress throughout the world to produce high performance catalysts for achieving, with minimum ozone consumption, total mineralization of organic contaminants, when required, more particularly in drinking or medicinal purposes, provided that consecutive removal of S, N and other derivatives is performed. The required catalyst quantity depends on its very chemical structure and that of the organic molecules to be eliminated. For instance, ozonation requires an optimum concentration of CuS-based catalyst of 400 mg.L^{-1} for treating textile dye-containing waters (Yong *et al.*, 2005), but of 500 mg.L^{-1} of ZnO nanoparticles for the decomposition of dichloroacetic acid (Zhai *et al.*, 2010). Municipal sewage treatment can be efficiently achieved with only 70 mg.L^{-1} of TiO_2 (Shivaraju, 2011).

In radical mechanism pathways, like that involved in Fenton processes, the optimum amount of free Fe^{2+} cations needed was explained by the occurrence of scavenging reactions between these ions and hydroxyl radicals (Daud *et al.*, 2010; Martins *et al.*, 2010). When using ash-supported Fe^{2+} cations, the detrimental effect of excessive catalyst amounts with respect to the optimum value may be explained in terms of reduced contact surface through particle aggregation into clusters (Flores *et al.*, 2008). In clay minerals (Azzouz, 2012; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014), such a phenomenon was attributed to the fact that high catalyst concentrations

enhance clay-clay interactions at the expense of those occurring between clay lamella and zone and (or) the organic substrates.

In oxidation processes, the effectiveness of solid catalysts is expected to decrease in time with increasing number of reuses (Shivaraju, 2011; Sun *et al.*, 2005). In some cases, this must be due to unavoidable alteration by leaching of the catalyst surface, more particularly in excessively acidic or alkaline media. Leaching is often observed in ion-exchanged catalysts such as zeolites and clay minerals. On hybrid organic-inorganic catalysts such as metal-containing polyamidoxime grafted on starch, the activity decay was explained by a possible accumulation of the reaction products on the organic moiety (Elhamshary *et al.*, 2011). Nonetheless, the authors of this work did not emphasize on the possible oxidative decomposition of the organic moiety of the solid catalyst.

For aluminosilicates such clay minerals, cation losses, even in moderately acidic media, were already reported (Azzouz, 2012; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014). Improvement attempts have suggested catalyst refreshing through periodical ion-exchange treatments for maintaining the catalytic activity for more than fifty cycles (Shahidi *et al.*, 2014). Such a treatment targets a re-saturation of the exchangeable sites with metal cations. Investigations are still in progress in this regard.

In many cases, slight heating, more particularly between 10 °C to 20 °C, was found to enhance the catalytic activity in oxidative degradation processes of organic molecules (Daud *et al.*, 2010; Ramirez *et al.*, 2010; Yong *et al.*, 2005; Elhamshary *et al.*, 2011; Chedeville *et al.*, 2005). This was usually explained in terms of an acceleration of the reactions that generate $^{\bullet}OH$ radicals (Yong *et al.*, 2005). However,

in some cases, excessive temperature increase is expected to produce detrimental effects, by reducing the ozone solubility in water. This explains why, in most cases, room temperature is regarded as being optimum, more particularly for catalytic ozonation (Legube and Karpel Vel Leitner, 1999; Azzouz, 2012; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014; Sun *et al.*, 2005). Similar observations were made when performing the ozonation of dimethylphthalate over Fe/SBA-15 (Huang *et al.,* 2011), of *p*-chlorobenzoic acid over Fe/MCM-41 catalyst (Huang *et al.,* 2012), or of oxalic acid on MWCNTs (Liu *et al.*, 2011). Nevertheless, such a detrimental effect of temperatures higher than the ambient values may also be explained by a possible acceleration of the decomposition of radicalic species, if any, or an attenuation of reagent adsorption on the surface of the solid catalyst (Shahidi *et al.*, 2014). Besides, higher temperatures may also produce undesired pH modification constraints for process monitoring.

2.6.2 Correlation between catalysts and pH

In processes involving oxidizing agents and more particularly radicals, the pH level of the reaction mixture is expected to strongly influence the mechanisms pathway (Azzouz *et al.*, 2010; Shahidi *et al.*, 2014). High pHs are known to promote the formation of hydroxyl radicals, as noticed in a wide variety of oxidation processes, more particularly in the ozonation of phenol on activated carbon (Ulson *et al.*, 2012) and on starch-supported metal-containing polyamidoxime (Elhamshary *et al.*, 2011), or in the oxidative elimination of methylene blue on zeolite (Valdesa *et al.*, 2009).

In the ozonation of dichloroacetic acid on ZnO nanoparticles, alkaline pHs were found to produce much higher degradation yield, due the formation of negatively charged ZnO^- species, as compared to pH 2, which gave oxidation yield ca. 6 times

lower (Zhai *et al.*, 2010). This detrimental effect of low pH was explained in terms of a predominance of scavenging effect of H^+ ions on the produced hydroxyl radicals in acidic media. Additional arguments in this regard are provided by attempts in the photo-catalytic oxidation of organic compounds (Shivaraju, 2011), more particularly when using TiO_2 as catalyst, where high degradation yield were obtained in conditions favoring the production of hydroxyl radicals (Piera *et al.*, 2000). The catalytic ozonation of nitrobenzene on ceramic honeycomb produced almost total decomposition after 10 minutes at pH 9. At acidic pH values the degradation yield did not exceeded 20% (Sun *et al.*, 2005). However, alkaline pH may also cause detrimental changes in the structure of some catalyst surfaces mainly through precipitation processes, as observed for ion-exchanged montmorillonite (Azzouz *et al.*, 2010).

In the presence of supported cations (Ramirez *et al.*, 2010), a Fenton-like catalytic oxidation produced an almost total decomposition of phenol at acidic pH of 2.5-3.0. Such pH levels are supposed to promote the production of oxonium ions ($H_3O_2^+$) (Daud *et al.*, 2010). However, at acidic pHs, care should be taken to prevent catalyst decomposition, more particularly when using aluminosilicates, which may undergo dealumination.

In moderately acidic pHs around 3, appreciable decomposition yields are also possible, as observed in the photocatalytic ozonation of pyrrole-2-carboxylic acid (Gilbert, 2002) and the catalytic ozonation of *p*-chlorobenzoic acid and phenanthrene on ferric oxyhydroxide (FeOOH) (Park *et al.*, 2002). As previously stated for ozonation in the presence of ion-exchanged montmorillonite (Azzouz, 2012; Azzouz *et al.*, 2010; Shahidi *et al.*, 2014) intermediate pH values ranging from 2.5 to 4.5 appear to involve a synergistic effect between adsorption and oxidation, and between ozonation on the catalyst surface and in bulk solution.

In most cases, the oxidizing capacity of ozone is considerably attenuated and sometimes even suppressed at neutral pHs. For certain catalysts, pH values around neutral produce the lowest activity regardless to the catalyst used (Shivaraju, 2011; Shahidi *et al.*, 2014). This must be due to the occurrence of pH threshold involving changes in the mechanism pathway. Around pH 6-8, the reactive and catalytic species involved in both acidic and alkaline pHs must display the lowest concentrations in the reaction mixtures. Under these conditions, any slight pH change may produce pronounced detrimental interactions between the species present in small amounts in the liquid media. In all cases, changes in pHs unavoidably take place during oxidation reactions, due to the formation of intermediates and accumulation of short-chain carboxylic acids (Fontanier *et al.*, 2005; Martins and Quinta- Ferreira, 2009; Järvik *et al.*, 2010). This explains somehow, and at least partly, the decay in time of the catalytic activity during most oxidation process supposed to be favored by moderately acidic pHs.

The effect of pH variations should be strongly correlated to the presence and structures of the catalysts employed. These pH changes may be enhanced by the presence of catalyst, which, in turn, may undergo modifications in both chemical composition and surface properties. Such modifications are specific to each type of catalyst. For instance, the non-catalytic ozonation of textile dyes showed high efficiency at alkaline pHs, due to the production of hydroxyl radicals, but this performance shift to moderately acidic pHs when using CuS as catalyst (Pirgalioglu and Ozbelge, 2009).

This clearly indicates that non catalytic ozonation does not proceed via the same pathway as in the presence of catalyst, and that the concept of optimum pH for high radical production, if any, is specific to each type of catalysts (Yong *et al.*, 2005). For instance, volcanic sand acted as effective catalyst in the ozonation of benzothiazole at

pH 7, due to the predominant contribution of a radical mechanism (Valdes *et al.*, 2008). Effective radical mechanisms seem to be involved at pH 10 in the ozonation of aromatic compounds in the presence of porous manganese and cobalt-modified diatomaceous materials (Li *et al.*, 2010), but only at pH 4 in the catalytic ozonation of molasses on SnO_2 (Zeng *et al.*, 2009). On solid catalysts, the optimum pH values should be correlated to the acid-base interaction between the catalyst surface and the dispersed species. Here, the concentrations of ozone (Ping *et al.*, 2002) and of the organic substrates (Yong *et al.*, 2005) along with the very acid-base properties of the catalyst surfaces (Azzouz *et al.*, 2010; Valdesa *et al.*, 2009) must play significant roles, more particularly in reagent adsorption. Elucidation of the roles of acid-base interactions between all the species dispersed in the liquid media imposes intensive investigations in this regard.

2.7 Conclusion

The data examined in this chapter allow concluding that effective water treatments without traces of persistent hazardous by-products or toxins can be achieved through suitable oxidative processes. The results obtained after intensive research have succeeded in imposing a new ecologic vision in designing complete oxidative treatments of wastewaters, at least for specific water uses. In this regard, the total absence of any traces of organic by-products has progressively become a major issue to be addressed. In other words, a wide variety of catalysts are now studied for improving oxidative degradations of organic contaminants in aqueous media. All these studies has focused their interest towards thorough mineralization into inorganic final products that can be released in the environment (CO_2 and water), easily removed by re-dissolution in water (SOx, NOx and derivatives) or retreated into added-value derivatives. Nevertheless, notwithstanding the outstanding

achievements made in wastewater treatments, total removal of organic contaminants with low energy consumption and without generating traces of persistent toxins still remains a challenge difficult to achieve. This is mainly due to the refractory character towards oxidation of short chain derivatives, more particularly oxygenated compounds.

The data summarized herein show that, among all the research directions undertaken so far, those targeting the improvements of oxidative procedures, more particularly ozonation, are probably the most promising routes for economical, technological and ecological reasons. Some of these procedures, and most specifically solid-catalyzed ozonations under optimum conditions, have already made possible not only the total decomposition of organic compounds containing only hydrogen, carbon and oxygen atoms, but also the total mineralization of their by-products into carbon dioxide. A key-step in achieving such a performance resides in the rigorous choices of adequate solid catalysts to be used in optimum amount under optimum pH conditions, in correlation with the nature of the organic substrates to be decomposed. All these factors are supposed to produce a synergy in promoting suitable mechanism pathways that involve both adsorption and surface reaction for the oxidative degradation of a given organic substrate.

There are no common rules in adopting alkaline or acidic pHs for wastewater treatments. However, a deep analysis of the data examined allows stating that solid catalysts with ion exchange capacity are supposed to promote ozonation both on the catalyst surface and in the bulk solution in moderately acidic media. The kinetic study provided sufficient evidence in this regard. The oxidative techniques, including the catalyst types and concentrations and all the other parameters discussed herein should be selected according to the contaminant's nature and the acid-base properties of the every wastewater to be treated. For economical reasons, crystalline

aluminosilicates and more particularly clay minerals appear as promising catalyst supports for such purposes. Through judicious and convenient modifications, their acid-base properties, adsorption capacity, affinity towards reagents and others can be willingly modulated for specific applications in the treatment of specific organic contaminants in specific wastewaters. This possibility to control the clay mineral catalytic activity opens new prospects in wastewater treatments for producing clean waters without any traces of harmful and toxic derivatives. In the next chapters, we will design some experiments to verify the effectiveness of the clay based catalysts to mineralize organic pollutants and obtain the optimum working conditions to achieve total mineralization.

REFERENCES

Akhtar, J., Amin, N.-A.-S. and Aris, A. (2011). Combined adsorption and catalytic ozonation for removal of sulfamethoxazole using Fe_2O_3/CeO_2 loaded activated carbon. *Chemical Engineering Journal*, 170, 136–144.

Azzouz, A. (2012). Advances in Oxidative Decomposition of Oxalic Acid in Aqueous Media, in: J. C. Taylor (Eds.), Advances in Chemistry Research (p. 1 – 31). New York :Nova-Publishers.

Azzouz, A., Kotbi, A., Niquette, P., Sajin, T., Ursu, A.-V., Rami, A., Monette, F. and Hausler, R. (2010). Ozonation of oxalic acid catalyzed by ion-exchanged montmorillonite in moderately acidic media. *Reaction Kinetics Mechanisms and catalysis*, 99, 289 – 302.

Bahranowski, K., Gasior, M., Kielski, A., Podobinski, J., Serwicka, E.-M., Vartikian, L.-A. and Wodnicka, K. (1999). Copper-doped montmorillonites of toluene and alumina-pillared as catalysts for oxidation xylenes with hydrogen peroxide. *Clay Minerals*, 34, 79 – 87.

Barbunsinski, K. (2009). Fenton Reaction - Controversy Concerning The Chemistry. *Ecological Chemistry and Engineering*, 16, 347 – 358.

Barrault, J., Abdellaoui, M., Bouchoule, C., Majesté, A., Tatibouët, J.-M., Louloudi, A., Papayannakos, N. and Gangas, N.-H. (2000). Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays. *Applied Catalysis B: Environmental,* 27, L225–L230.

Bayati, F., Shayegan, J., Shokrollahi, H. and Parsa, J.-B. (2009). Removal of Organic Pollutants from wastewater streams by Dissolved Air Precipitation/ Solvent Sublation. *Chemical Engineering Transactions*, 17, 257 – 262.

Beltran, F.J., Rivas, F.J. and Gimeno, O. (2005). Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water. *Journal of Chemical Technology and biotechnology*, 80, 973–984.

Bergaya, F., Theng, B.-K.-G., Lagaly, G. (2006). Handbook of Clay Science (p. 541–546). Oxford : Elsevier.

Bin, A.-K. and Madej, S.-S. (2012). Comparison of the Advanced Oxidation Processes (UV, $UV/H_2O_2$and O_3) for the Removal of Antibiotic Substances during Wastewater Treatment. *Ozone: Science and Engineering,* 34, 136–139.

Boufatita, M., Amar, H.-A. and McWhinnie, W.-R. (2008). Development of an algerian material montmorillonite clay — Intercalation with selective long chain alkylammonium cations (Octadecytrimethylammonium, Cetylpyridium and Tetrabutylammonium) and with tellerium complexes. *Desalination*, 223, 366–374.

Can, Z.-S. and Gurol, M. (2003). Formaldehyde Formation During Ozonation Of Drinking Water, *Ozone: Science and Engineering* , 25, 41 – 51.

Canton, C., Esplugas, S. and Casado, J. (2003). Mineralization of phenol in aqueous solution by ozonation using iron or copper salts and light. *Applied Catalysis B: Environmental*, 43, 139–149.

Chedeville, O., Bayraktar, A.-T. and Porte, C. (2005). Modeling of Fenton Reaction for theOxidation of Phenol in Water. *Journal of Automated Methods and Management in Chemistry*, 2, 31–36.

Chen, Y.-H., Hsieh, D.-C. and Shang, N.-C. (2011). Efficient mineralization of dimethyl phthalate by catalytic ozonation using TiO_2/Al_2O_3 catalyst. *Journal of Hazardous Matererials,* 192, 1017– 1025.

Cooper, C. and Burch, R. (1999). An Investigation of Catalytic Ozonation for the Oxidation of Halocarbons in Drinking Water Preparation. *Water Research*, 33, 3695 – 3700.

Daneshvar, N., Aber, S., Dorraji, M.-S., Khataee, A.-R. and Rasoulifard, M.-H. (2008). Preparation and Investigation of Photocatalytic Properties of ZnO Nanocrystals: Effect of Operational Parameters and Kinetic Study. *International Journal of Chemical and Biological Engineering*, 1, 23 – 28.

Daud , N.K., Ahmad , M.A. and Hameed , B.H. (2010). Decolorization of Acid Red 1 dye solution by Fenton-like Process Using Fe–Montmorillonite K10 Catalyst. *Chemical Engineering Journal*, 165, 111–116.

Diez, M.C. (2010). Biological aspects involved in the degradation of organic pollutants. *Journal of plant Nutrition and Soil Science,* 10, 244 – 267.

Dong, Y.-M., Wang, G.-L., Jiang, P.-P., Zhang, A.-M., Yue, L., Zhang, X.-M. (2011). Simple preparation and catalytic properties of ZnO for ozonation degradation of phenol in water. *Chinese Chemical Letters*, 22, 209–212.

Elhamshary, H., Elnewehy, M.-H., and Aldeyab, S.-S. (2011). Oxidation of Phenol by Hydrogen Peroxide Catalyzed by Metal-Containing Poly(amidoxime) Grafted Starch. *Molecules*, 16, 9900 – 9911.

Elsousy, K., Hussen, A., Hartani, K. and Elaila, H. (2007). Elimination of Organic Pollutants using Supported Catalysts with Hydrogen Peroxide. *Jordan Journal of Chemistry*, 2, 97 – 103.

Flores, Y., Flores, R. and Gallegos, A.-A. (2008). Heterogeneous catalysis in the Fenton-type system reactive black $5/H_2O_2$. *Journal of Molecular Catalysis A: Chemical*, 281, 184–191.

Fontanier, V., Farines, V., Albet, J., Baig, S. and Molinier, J. (2005). Oxidation of Organic Pollutants of Water to Mineralization by Catalytic Ozonation. *Ozone: Science and Engineering* 27, 115–128.

Gilbert, E. (2002). Influence of Ozone on the Photocatalytic Oxidation of Organic Compounds. *Ozone: Science and Engineering,* 24, 75 – 82.

Giordano, G., Perathoner, S., Centi, G., De Rosa, S., Granato, T., Katovic, A., Siciliano, A., Tagarelli, A. and Tripicchio, F. (2007). Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts. *Catalysis Today* 124, 240–246.

Goncalves, A., Albero, J.-S., Fernández, E.-V.-R., Carlos, J., Ruiz, S., Orfaoa, J.-J.M., Escribano, A.-S. and Pereira, M.-F.-R. (2012). Highly dispersed ceria on activated carbon for the catalyzed ozonation of organic pollutants. *Applied Catalysis B: Environmental,* 113– 114, 308– 317.

Goncalves, A.-A. and Gagnon, G.-A. (2012). Recent Technologies for Ballast Water Treatment. *Ozone: Science and Engineering,* 34, 174–195.

Gul, S., Ozcan, O. and Erbatur, O. (2007). Ozonation of C.I. Reactive Red 194 and C.I. Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon. *Dyes and Pigments,* 75, 426 – 431.

Guo, Y., Yang, L., Cheng, X. and Wang X. (2012). The Application and Reaction Mechanism of Catalytic Ozonation in Water Treatment. *Journal of Environmental and Analytical Toxicology,* 2, 1–6.

Hassana, M.-M. and Hawkyard, C.-J. (2002). Ferral-catalyzed ozonation of aqueous dyes in a bubble-column reactor. *Catalysis Communications,* 3, 281–286.

Henry , M.-T. and Beaudry, J.-P. (1984). Chimie des Eaux (p. 56 – 81). Sainte – Foy : Le griffon d'argile Inc.

Huang, R., Yan, H., Li, L., Deng, D., Shu, Y. and Zhang, Q. (2011). Catalytic activity of Fe/SBA-15 for ozonation of dimethyl phthalate in aqueous solution. *Applied Catalysis B: Environmental,* 106, 264– 271.

Huanga, R., Lan, B., Chen, Z., Yan, H., Zhang, Q., bing, J. and Li, L. (2012). Catalytic ozonation of p-chlorobenzoic acid over MCM-41 and Fe loaded MCM-41. *Chemical Engineering Journal*, 180 (2012) 19– 24.

Ito, H., Kotake, T. and Masai, M. (1996). In vitro Degradation of oxalic acid by human feces. *International Journal of Urology*, 3, 207–211.

Iurascu, B., Siminiceanu, I., Vione, D., Vicente, M.-A. and Gil, A. (2009). Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. *Water Research*, 43, 1313–1322.

Jagtap, N., and Ramaswamy, V. (2006). Oxidation of aniline over titania pillared montmorillonite clays. *Applied Clay Science*, 33, 89–98.

Järvik, O., Kamenev, I., Viiroja, A. and Kallas, J. (2010). Purification of Phenolic Wastewater Using Aerobic Bio-oxidation Combined with Activated Carbon Treatment and Ozonation. *Ozone: Science and Engineering,* 32, 417–423.

Joshia, G.-V., Kevadiya, B.-D., Patel, H.-A., Bajaj, H.-C. and Jasra, R.-V. (2009). Montmorillonite as a drug delivery system: Intercalation and in vitro release of timolol maleate, *International Journal of Pharmaceutics,* 374, 53–57.

Kanel, S.-R., Nappolian, B., Choi, H. and Yang, J.-W. (2003). Heterogeneous Catalytic Oxidation of phenanthrene by Hydrogen Peroxide in soil slurry: Kinetics , mechanism and implication. *Soil and Sediment contamination*, 12, 101 – 117.

Kasprzyk-Hordern, B., Zioek, M. and Nawrocki, J. (2003). Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Applied Catalysis B: Environmental*, 46, 639–669.

Kaur, N. and Kishore, D. (2012). Montmorillonite: An efficient, heterogeneous and green catalyst for organic synthesis. *Journal of Chemical and Pharmaceutical Research*, 4, 991 – 1015.

Khankhasaeva, S.T., Bryzgalova, L.V., Dashinamzhilova, E.T. and Ryazanttsev, A.A. (2004). Fe-Montmorillonites in the reaction of organic dyes oxidation. *Chemistry for Sustainable Development,* 12, 713 –717.

Kjellström, T., Lodh, M., McMichael, T., Ranmuthugala, G., Shrestha, R. and Kingsland, S. (2006). Disease Control Priorities in Developping Countries, (p. 817 – 833). Washington DC: oxford university press.

Koohestanian, A., Hosseini, M. and Abbasian, Z. (2008). The Separation Method for Removing of Colloidal Particles from Raw Water. *American-Eurasian journal of agricultural and environmental*, 4, 266 – 273.

Kumar, P. and Sathyamurthy, N. (2013). An ab initio quantum chemical investigation of the structure and stability of ozone-water complexes. *Chemical Physics*, 415, 214 – 221.

Kwong, C.W., Chao, C.Y., Hui, K.-S. and Wan, M.P. (2008). Removal of VOCs from indoor environment by ozonation over different porous materials. *Atmosphetic Environment*, 42, 2300–2311.

Kwong, C.W., Chao, C.Y.H., Hui, K.-S. and Wan, M.P. (2008). Catalytic Ozonation of Toluene Using Zeolite and MCM-41 Materials. *Environmental Science & Technology*, 42, 8504–8509.

Legube, B. and Karpel Vel Leitner, N. (1999). Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catalysis Today,* 53, 61–72.

Lei, Z., Ma, G. and Jia, C. (2007). Montmorillonite (MMT) supported tin (II) chloride: An efficient and recyclable heterogeneous catalyst for clean and selective Baeyer–Villiger oxidation with hydrogen peroxide, *Catalysis Communications*, 8, 305–309.

Leitner, N.K.V., Acedo, F.-B. and Delanoe, B.L. (2000). Reactivity of various catalysts during ozonation of succinic Ru/CeO2 acid aqueous solutions. *New Journal of Chemistry*, 24, 229 – 233.

Li, B., Xu, X., Zhu, L., Ding, W. and Mahmood, Q. (2010). Catalytic ozonation of industrial wastewater containing chloro and nitro aromatics using modified diatomaceous porous filling, *Desalination,* 254, 90–98.

Li, L., Ye, W., Zhang, Q., Sun, F., and Lu, P. (2009). Catalytic ozonation of dimethyl phthalate over cerium supported on activated carbon. *Journal of Hazardous Matererials*, 170, 411–416.

Li, Y.-F., Scholtz, M.-T. and Van Heyst, B.-J. (2012). Global gridded emission inventories of α-hexachlorocyclohexan. *Journal of Geophysical Research*, 105 (D5), 6621–6632.

Lin, F.-H., Lee, Y.-H., Jian, C.-H., Wong, J.-M., Shieh, M.-J. and Wang, C.-Y. (2002). A study of purified montmorillonite intercalated with 5-fluorouracil as drug carrier. *Biomaterials*, 23, 1981–1987.

Lin, J., Nakajima, T., Jomoto, T. and Hiraiwa, K. (2000). Effective Catalysts for Wet Oxidation Of Formic acid by oxigene and ozone. *Ozone: Science and Engineering,* 22, 241 – 247.

Liotta, L.-F., Gruttadauria, M., DiCarlo, G., Perrini, G. and Librando, V. (2009). Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity, *Journal of Hazardous Matererials,* 162, 588–606.

Liu, C., Tanaka, H., Zhang, L., Zhang, J., Huang, X., Ma, J. and Matsuzawa, Y. (2012). Fouling and structural changes of Shirasu porous glass (SPG) membrane used in aerobic wastewater treatment process for microbubble aeration. *Journal of Membrane Science*, 421–422, 225 – 231.

Liu, Z.-Q., Ma, J., Cui, Y.-H., Zhao, L. and Zhang, B.-P. (2011). Factors affecting the catalytic activity of multi-walled carbon nanotube for ozonation of oxalic acid. *Separation and Purification Technology*, 78, 147–153.

Lv, A., Hu, C., Nie, Y. and Qu, J. (2010). Catalytic ozonation of toxic pollutants over magnetic cobalt and manganese co-doped γ-Fe_2O_3. *Applied Catalysis B: Environmental,* 100, 62–67.

Maldonado, M.-I., Malato, S., Estrada, L.-A.-P., Gernjak, W., Oller, I., Domenech, X. and Peral, J. (2006). Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor. *Journal of Hazardous Matererials B*, 138, 363–369.

Mantzavinos, D. (2003). Removal of Benzoic Acid Derivatives From Aqueous Effluents by The Catalytic Decomposition of Hydrogen Peroxide. *Institution of Chemical Engineers,* 81, 99 – 106.

Martins, R.-C. and Quinta- Ferreira, R.-M. (2009). Screening of Ceria-Based and Commercial Ceramic Catalysts for Catalytic Ozonation of Simulated Olive Mill Wastewaters. *Industrial & Engineering Chemistry Research*, 48, 1196–1202.

Martins, R.-C., Silva, N.-A. and Ferreira, R.-M.-Q. (2010). Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal, *Applied Catalysis B: Environmental*, 99, 135–144.

Matheswaran, M., Balaji, S., Chung, S.-J. and Moon, I.S. (2007). Studies on cerium oxidation in catalytic ozonation process: A novel approach for organic mineralization. *Catalysis Communications*, 8, 1497–1501.

Mohan, S.M. (2014). Use of naturalized coagulants in removing laundry waste surfactant using vario us unit processe s in lab-scale. *Journal of environmental Management*, 136, 103 – 111.

Munter, R. (2001). Advanced Oxidation Processes – Current Status and Prospects. *Estonian Academy of science. Chemistry*, 50, 59–80.

Munter, R., Trapido, M., Veressinina, Y. and Goi, A. (2006). Cost Effectiveness of Ozonation and AOPs for Aromatic Compound Removal from Water: A Preliminary Study. *Ozone: Science and Engineering* , 28, 287–293.

Murray, H. (2007). Applied Clay Mineralogy (p. 161 –178). Bloomington : Elsevier.
Nagendrappa, G. (2002). Organic Synthesis using Clay Catalysts. *Resonance*, 7, 64 – 71.

Nawrocki, J. and Kasprzyk-Hordern, B. (2010). The efficiency and mechanisms of catalytic ozonation, *Applied Catalysis B: Environmental*, 99, 27–42.

Negrel, P., Blessing, M., Millot, R., Giraud, E.P. and Innocent, C. (2012). Isotopic methods give clues about the origins of trace metals and organic pollutants in the environment. *Trends in Analitical Chemistry*, 38, 143 – 153.

Neitner, N.-K.-V., Délouane, B., Legube, B. and Luc, F. (1999). Effect of catalysts during ozonation of Salysilic acid, Peptides and Humic Substances in Aquous Solution. *Ozone: Science and Engineering*, 21, 261 –276.

Nidheesh , P.V. and Gandhimathi, R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination* , 299, 1 – 15.

Nollet, L. (2007). Handbook of water Analysi (p. 300 – 302). New York : Marcel Dekker Inc.

Northcott, G.-L. and Jones, K.-C. (2003). Validation of Procedures to Quantify Nonextractable Polycyclic Aromatic Hydrocarbon Residues in Soil. *Journal of Environmental Quality*, 32, 571 – 582.

Numata, M., Yarita, T., Aoyagi, Y., Yamazaki, M. and Takatsu, A. (2005). Investigation of saponification for determination of polychlorinated biphenyls in marine sediments. *Chemosphere,* 58, 865–875.

Orge, C.-A., Orfao, J.-J.-M. and Pereira, M.-F.-R. (2011). Catalytic ozonation of organic pollutants in the presence of cerium oxide–carbon composites. *Applied Catalysis B: Environmental,* 102, 539–546.

Orge, C.-A., Orfao, J.-J.-M., and Pereira, M.-F.-R. (2012). Composites of manganese oxide with carbon materials as catalysts for the ozonation of oxalic acid. *Journal of Hazardous Matererials,* 213– 214, 133– 139.

Orge, C.-A., OrfaoJ.-J.-M., Pereira, M.-F.-R., Duarte de Farias, A.-M., Rabelo Neto, R.-C. and Fraga, M.-A. (2011). Ozonation of model organic compounds catalysed by nanostructured cerium oxides. *Applied Catalysis B: Environmental,* 103, 190–199.

Pang, Y.-L., Abdullah, A.-Z. and Bhatia, S. (2011). Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. *Desalination*, 277, 1 – 14.

Park, J.-S., Choi, H. and Ahn, K.-H. (2002). The reaction mechanism of catalytic oxidation with hydrogen peroxide and ozone in aqueous solution. *Water Science and Technology*, 47, 179–184.

Piera, E., Calpe, J.-C., Brillas, E., Domènech, X. and Peral, J. (2000). 2,4-Dichlorophenoxyacetic acid degradation by catalyzed ozonation:TiO_2/UVA/O_3 and Fe(II)/UVA/O_3 systems. *Applied Catalysis B: Environmental,* 27, 169–177.
Pillai, U.-R., Demessie, E.-S. (2003). Oxidation of alcohols over Fe^{3+} /montmorillonite-K10 using hydrogen peroxide. *Applied Catalysis A: General*, 245, 103–109.

Ping, T.-S., Hua, L.-W., Qing, Z.-J. and Nan, C.-C. (2002). Catalytic Ozonation of Sulfosalicylic Acid. *Ozone: Science and Engineering*, 24, 117 – 122.

Pirgalioglu, S. and Ozbelge, T.-A. (2009). Comparison of non-catalytic and catalytic ozonation processes of three different aqueous single dye solutions with respect to powder copper sulfide catalyst. *Applied Catalysis A: General,* 363, 157–163.

Rahni , M. and Legube, B. (1996). Mechanism of salicylic acid precipitation by Fe(III) coagulation. *Water Research*, 30, 1149 – 1160.

Ramirez, J.H., Costa, C.-A., Madeira, L.-M., Mata, G., Vicente, M.-A., Cervantes, M.-L.-R., Peinado, A.-J.-L. and Aranda, R.-M.-M. (2007). Fenton-like oxidation of Orange II solutions using heterogeneous catalysts based on saponite clay. *Applied Catalysis B: Environmental*, 71, 44–56.

Ramirez, J.H., Vicente, M.A. and Madeira, L.M. (2010). Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment. *Applied Catalysis B: Environmental*, 98, 10–26.

Ren, L., Li, G., Han, Y.-C., Jiang, D.-H. and Huang, H.-C. (2007). Degradation of oxalic acid by Coniothyrium minitansand its effects on production and activity of β-1,3-glucanase of this mycoparasite. *Biological Control*, 43, 1–11.

Rice, R.-G., Netzer, A. and Arbor, A. (1982). Hand book of ozone technology and application (p. 255 – 285). Michigan : Science publishers.

Rubin, M.-B. (2008). The Histry of Ozone, Ozone on Silica Gel. *Bulletin for the History of Chemistry*, 33, 68 – 75.

Shahidi, D., Roy, R., and Azzouz, A. (2014). Total removal of oxalic acid via synergistic parameter interaction in montmorillonite catalyzed ozonation. *Journal of Environmental Chemical Engineering*, 2, 20-30.

Shiraga, M., Kawabata, T., Li, D., Shishido, T., Komaguchi, K., Sano, T. and Takehira, K. (2006). Memory effect-enhanced catalytic ozonation of aqueous phenol and oxalic acid over supported Cu catalysts derived from hydrotalcite. *Applied Clay Science*, 33, 247–259.

Shivaraju, H.-P. (2011). Removal of Organic Pollutants in the Municipal Sewage Water by TiO_2 based Heterogeneous Photocatalysis. *International Journal of Environmental Science*, 1, 911 – 923.

Singh, C., Chaudhary, R. and Thakur, R.-S. (2011). Performance of advanced photocatalytic detoxification of municipal wastewater under solar radiation. *International Journal of Energy and Environmental*, 2, 337 – 350.

Stasinakis, A.-S. (2008). Use of Selected Advanced Oxidation Processes (AOPs) for Wastewater Treatment. *Global NEST Journal*, 10, 376 – 385.

Stuber, F., Font, J., Fortuny, A., Bengoa, C., Eftaxias, A. and Abregat, A. (2005). Carbon materials and catalytic wet air oxidation of organic pollutants in wastewater. *Topics in Catalysis*, 33, 3 –50.

Sui, M., Duan, B., Sheng, L., Huang, S. and She, L. (2012). Catalytic Performance of Layered Double Hydroxides Co-Mn-Al for Ozonation of Organic Pollutants in Water. *Chinese Journal of Catalysis*, 33, 1284–1289.

Sui, M., Liu, J. and Sheng, L. (2011). Mesoporous material supported manganese oxides (MnOx/MCM-41) catalytic ozonation of nitrobenzene in water. *Applied Catalysis B: Environmental*, 106, 195– 203.

Sui, M., Xing, S., Sheng, L., Huang, S. and Guo, H. (2012). Heterogeneous catalytic ozonation of ciprofloxacin in water with carbon nanotube supported manganese oxides as catalyst. *Journal of Hazardous Matererials,* 227– 228, 227– 236.

Sun, Z.-Z., Ma, J., Wang, L.-B. and Zhao, L. (2005). Degradation of nitrobenzene in aqueous solution by ozone ceramic honycomb. *Journal of Environmental Science,* 17, 716 – 721.

Tizaoui, C., Bickley, R.-I., Slater, M.-J., Wang, W.-J., Ward, D.-B. and Aljaberi, A. (2008). A comparison of novel ozone-based systems and photocatalysis for the removal of water pollutants. *Desalination*, 227, 57 – 71.

Trapido, M., Veressinina, Y., Munter, R. and Kallas, J. (2005). Catalytic Ozonation of m-Dinitrobenzene. *Ozone: Science and Engineering,* 27, 359–363.

Ulson, S.-M.-A., and Souza, F.-B., Souza, A.-A.-U. (2012). Application of Individual and Simultaneous Ozonation and Adsorption Processes in Batch and Fixed-Bed Reactors for Phenol Removal. *Ozone: Science and Engineering,* 34, 259–268.

Valdes, H., Murillo, F.-A., Manoli, J.-A. and Zaror, C.-A. (2008). Heterogeneous catalytic ozonation of benzothiazole aqueous solution promoted by volcanic sand. *Journal of Hazardous Matererials,* 153, 1036–1042.

Valdesa, H., Farfan, V.-J., Manoli, J.-A. and Zaror, C.-A. (2009). Catalytic ozone aqueous decomposition promoted by natural zeolite and volcanic sand. *Journal of Hazardous Matererials,* 165, 915–922.

Volk, C., Roche, P., Joret, J.-C. and Paillard, H. (1997). Comparision of the effect of ozone, ozone – hydrogen peroxidesystem and catalytic ozone on the biodegradable organic matter of a fulvic acid solution. *Water Research,* 31, 650 – 656.

Wang, D. and Fiessel, W. (2008). Evaluation of media for simultaneous enumeration of total coliform and Escherichia coli in drinking water supplies by membrane filtration techniques. *Journal of Environmental Science*, 20, 273–277.

Wu, C.-H., Kuo, C.-Y. and Chang, C.-L. (2008). Decolorization of C.I. Reactive Red 2 by Catalytic Ozonation Processes. *Journal of Hazardous Materials,* 153, 1052–1058.

Ye, M., Chen, Z., Liu, X., Ben, Y. and Shen, J. (2009). Ozone enhanced activity of aqueous titanium dioxide suspensions for photodegradation of 4-chloronitrobenzene. *Journal of Hazardous Matererials*, 167, 1021–1027.

Yong, K., Wu, J. and Andrews, S. (2005). Heterogeneous Catalytic Ozonation of Aqueous Reactive Dye. *Ozone: Science and Engineering,* 27, 257–263.

Zeng, Y.-F., Liu, Z.-L. and Qin, Z.-Z. (2009). Decolorization of molasses fermentation wastewater by SnO_2-catalyzed ozonation. *Journal of Hazardous Matererials,* 162, 682–687.

Zhai, X., Chen, Z., Zhao, S., Wang, H. and Yang, L. (2010). Enhanced ozonation of dichloroacetic acid in aqueous solution using nanometer ZnO powders. *Journal of Environmental Science,* 22, 1527–1533.

Zhang , W., Hou, F., Peng, Y., Liu, Q. and Wang, S. (2014). Optimizing aeration rate in an external nitrification–denitrifying phosphorus removal system for domestic wastewater treatment. *Chemical Engineering Journal*, 245, 342 – 347.

Zhao, L., Sun, Z., Ma, J. and Liu, H. (2009). Enhancement Mechanism of Heterogeneous Catalytic Ozonation by Cordierite-Supported Copper for the Degradation of Nitrobenzene in Aqueous Solution. *Environmental Science and Technology,* 43, 2047–2053.

CHAPTER III

TOTAL REMOVAL OF OXALIC ACID VIA SYNERGISTIC PARAMETER INTERACTION IN MONTMORILLONITE CATALYZED OZONATION

Abstract

Oxalic acid ozonation in water at room temperature produced decomposition yields of 50-100% in the presence of Na^{+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ion-exchanged montmorillonite as catalysts. Among these, Co(II)Mt and Fe(II)Mt produced the highest performances. The appreciable enhancement of oxalic acid removal as compared to homogenous ozonation and the ozonation yield decay upon heating suggest a significant contribution of adsorption. The initial pH of the reaction mixture, ozonation time and catalyst concentration showed strong influence. A 3^{k} factorial design with 27 ozonation attempts for each catalyst produced total removal of oxalic acid after 15 min at pH 2.87 with 1.88 $g.L^{-1}$ of Co(II)Mt, and pH 2.88 with 1.91 $g.L^{-1}$ of Fe(II)Mt. Because oxalic acid is well known to be a quite refractory intermediate in most oxidation attempts, these results suggest that total mineralization of any hazardous organic pollutants from aqueous media is possible in similar optimum conditions. Higher pH and catalyst amounts were detrimental, presumably due clay compaction, which is supposed to reduce the cation mobility and adsorption contribution. The initial pH was found to act also via synergistic interaction with the other parameters, presumably by enhancing clay exfoliation and adsorption of oxalate anion and ozone.

3.1 Introduction

Chemical, petrochemical, pharmaceutical and food industries, along with agriculture and forestry are major sources of organic pollutant in waste-waters (Nidheesh and Gandhimathi, 2012; Beltran *et al.*, 2005; (Giordano *et al.*, 2007). Primary treatments are not sufficiently effective because of residual traces of pollutants (Numata *et al.*, 2005; Northcott and Jones, 2003). Complete decomposition of organic pollutants requires powerful oxidative treatments to avoid the persistent presence of refractory short chain intermediates like oxalic acid (OA). The latter is known to display high chemical stability even in the so-called Advanced Oxidation Processes (AOPs). The main issue to be addressed is that the formation of OA is often the final stage in most oxidation methods (Garg and Mishra, 2013; Roy *et al.*, 2010; Santos *et al.*, 2005; Azzouz, 2012). Besides, OA is a hazardous compound (Azzouz *et al.*, 2010), and shows even more toxicity than most parent pollutants (Iurascu *et al.*, 2009).

Notwithstanding that some plants like rhubarb and sorrel contains OA, the latter is recognized as being quite poisonous to the kidneys (nephrotoxic), more particularly when present in drinking water. OA precipitation in the presence of calcium produces kidney stones, which contains calcium oxalate in a proportion of 80%. OA may even be fatal around a median lethal dose (LD50) of 375-380 mg/kg body weight for humans (Massey, 2003; Savage *et al.*, 2000; Savage, 2002; Savage *et al.*, 2004). In human and animal metabolism, OA may also form from excessive use of vitamin C, which is readily oxidized owing to its powerful antioxidizing capacity. This often results in gut lining irritation, rheumatoid arthritis, certain forms of chronic vulvar pains (vulvodynia) and other diseases (Azzouz *et al.*, 2010). However, being quite harmless in low doses, OA is rather regarded as being a precise indicator of incomplete oxidation of organic matter. For this reason, total mineralization of organic pollutants into carbon dioxide (CO_2) without generating any traces of OA or

any other short chain compounds has become an essential requirement for effective oxidative water treatments.

So far, attempts to OA oxidative mineralization into CO_2 have received fairly good attention in the published literature, and many advances have been made in this regard (Azzouz, 2012) Photocatalysis and Photoelectrocatalysis have long been considered promising approaches, but the incomplete decomposition of organic pollutants and high operating costs were still major obstacles for commercial applications (Nidheesh and Gandhimathi, 2012; Giordano *et al.*, 2007). AOPs resulted from continuous improvements of conventional oxidative methods (Beltran *et al.*, 2005). One of these, namely ozonation, more particularly at elevated pH, has focused interest. Nonetheless, no prospects can be envisaged as long as the issues related to the low solubility of ozone in the liquid media and its weak reactivity as compared to radical species still remain to be addressed. The use of metal cations produced higher effectiveness as compared to the non-catalytic routes, but water contamination by metals turned out to be a major drawback (Zhu and Xu, 2004; Pines and Reckhow, 2002; Bhattacharyya *et al.*, 1995). Significant improvements were registered in the presence of dispersed solid or supported catalysts. In this regard, ozonation on activated carbon produced almost total mineralization into carbon dioxide (Beltran *et al.*, 2002; Pinker and Henderson, 1996; Kaptijn, 1997; Jans and Hoigne, 1998). On solid catalysts, the ozonation process is expected to involve both surface phenomena and bulk water reactions between the organic substrate to be decomposed and oxidizing agents. Adsorption appears to play a key-role, because the catalytic activity was found to increase almost linearly with increasing catalyst surface area (Chatterjee *et al.*, 2006; Beltran *et al.*, 2002).

Among the wide variety of solid catalysts investigated so far, zeolites ion-exchanged with transition metal cations showed interesting performances (Park *et al.*, 2006).

However, more available and lower cost materials such as clay minerals appear to be more promising catalysts, which display almost similar surface properties as zeolites. Besides, their expandable structures allow them to be also used in the decomposition of large size substrates (Azzouz *et al.*, 2010; Zhu *et al.*, 1998; Dubey *et al.*, 2002; Ramaswamy *et al.*, 2002; Perathoner and Centi, 2005; Chung *et al.*, 2002). Previous attempts with ion-exchanged montmorillonite (Mt) revealed strong individual influences of pH, catalyst and ozone amounts on the decomposition yield (Azzouz *et al.*, 2010). Nevertheless, the role of the parameter interactions has never been tackled so far, and the occurrence of synergistic actions of ozone montmorillonite still remains to be elucidated. The core of the novelty of the present study resides in correlating these interactions with the contribution of the adsorption step through the role of pH in the global ozonation process. This issue has never been tackled and not even been envisaged so far.

For this purpose, montmorillonite ion-exchanged with Na^{+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations were employed as catalysts. OA ozonation in water was shown by a mathematical model using a 3^{k} factorial design of experiments for assessing the contributions of the interactions of the initial pH, ozonation time and catalyst amount. The synergy involving the ozonation reaction and adsorption will be discussed in terms of parameter interactions.

3.2 Materials and methods

3.2.1. Catalyst preparation and characterization

A crude bentonite (Sigma-Aldrich) was repeatedly impregnated with 2–5 M aqueous NaCl solutions at 80°C for 4-5 h, under vigorous stirring, until full ion exchange. After cooling overnight, the clay mineral suspension was repeatedly settled in distilled water at room temperature, under ultrasound exposure. Settling was performed overnight in a polyethylene cylinder obtained by cutting the tip of a large syringe (200mL). After supernatant removal, the resulting paste was then extruded, dried and fractionated. XRD analysis of the different fractions was used to select a montmorilonite-rich sample, designated as NaMt. The latter was repeatedly dialyzed overnight with distilled water in cellulose bags, until the total disappearance of the NaCl excess using the conventional $AgNO_3$ test. NaMt was then fully ion-exchanged through repetitive impregnations with aqueous solutions of transition metal salts under vigorous stirring. The resulting Fe(II)Mt, Fe(III) Mt, Co(II)Mt, Ni(II)Mt and Cu(II)Mt samples were then washed, dialyzed and air dried. These catalysts were characterized by Siemens D5000 X-ray diffractometer with CuK_α, λ=1.54051 A°, which revealed a broad 001 XRD reflexion for the crude bentonite, but sharp lines for the ion-exchanged montmorillonite samples. This is a common feature of homo-ionic clay minerals, which indicates a perfectly parallel arrangement of the clay sheets. Measurements via ammonium acetate saturation method (AMAS) and Kjeldahl ammonium distillation technique (Kitsopoulos, 1999) gave a cation exchange capacity (CEC) value of 100 meq/100 g. Deeper insights in the catalyst chemical composition were achieved before and after ozonation through thermogravimetric analyses (TGA) using a Seiko Instrument Inc. TG/DTA 6200 analyses carried out with thermal analyzer under a 120 $ml.min^{-1}$ air stream at 5 °C min^{-1} scanning rate and energy dispersion X-rays analysis (EDX with an EDAX-Sapphire instrument coupled to the

S-4300SE/N-VPSEM equipment , using a Si(Li) crystal and an active surface of 10 mm^2).

3.2.2. Ozonation of oxalic acid

Ozonation attempts were performed in a 2 cm x 30 cm cylindrical glass reactor, using 100 ml of O A solution with an initial concentration of 10^{-3} M (99.5% purity, supplied by Anachemia Canada Inc.) and various clay catalyst amounts. All experiments were performed in triplicate. Ozone was produced from pure oxygen (supplied by Paraxair Canada Inc.) by a Welsbacher ozone generator and injected into the batch reactor through a bubbler at 6 $mg.min^{-1}$. The ozonation experiments were performed at room temperature by bubbling ozone in an aqueous OA solution using two different procedures: (1) within a batch reactor, i.e. a flask coupled to a reflux cooling device to avoid liquid loss by evaporation. Periodic COD measurements were made for determining the remaining amount of unconverted OA. Here, small number of micro-samples were taken from the reaction mixture, so that the total amount removed (less than 10%) does not influence greatly the evolution in time of the ozonation process; (2) When higher number of samples is needed so as the total sample amount exceeds 10%, no sampling was made, and a series of small and similar reaction mixtures were simultaneous ozonated at the same ozone throughput for different bubbling times (Fig. S1). The samples were further analyzed through quantitative COD measurements and qualitative HPLC-MS identification of the reaction products and intermediates.

In order to ultimate studying of pH effect on the conversion of OA, the ozonation process was investigated at both intrinsic pH of the reaction mixture and different adjusted initial pH values. For this purpose pH was adjusted using concentrated

hydrochloric acid (36.5% purity) supplied by Caledon Ltd. and sodium hydroxide pills (95% purity) provided by Anachemia Canada Inc. An Accumet 15 pH meter was employed for pH measurements.

3.2.3 Products and intermediates analysis

The reaction mixture was qualitatively analyzed by liquid-chromatography-mass spectrometry (HPLC-MS Agilan-1200 instruments) using a C18 column and a 2:3 methanol:water mixture. After ozonation in optimum conditions, except carbonic acid and carbonates, no traces of any intermediate were detected. In other conditions traces formic and acetic acid were identified.

The OA conversion was evaluated by periodic measurements of the residual amount of unconverted reagent via a standard chemical oxygen demand technique (COD) (Liotta *et al.*, 2009). For this purpose, concentrated sulphuric acid (98% purity) supplied by Caledon Ltd., potassium dichromate 99.5%, iron(II) ammonium sulphate 99.5%, silver sulphate 99.5% and mercury(II) sulphate 99.5% all provided by Anachemia Canada Inc. were employed. The usual standard deviation (SD) in COD measurement is of 4-5%. However, the SD value was reduced to 1% thanks to the total absence of interfering agents such as halide anions and to the use of triplicate and different blanks, and even down to 1% through COD calibration curve obtained by the introduction of a correction factor assessed by HPLC.

3.3 Results and discussion

3.3.1 Effect of catalyst addition in oxalic acid ozonation

Preliminary observations showed that ozonation without catalyst produces low OA decomposition yield not exceeding 1-2% even after 60 min (Fig. 3.1). After addition of crude bentonite or NaMt, the OA conversion rose up to 5-6% and to almost 10%, respectively.

This provides clear evidence of the key-role of the solid surface on the ozonation process. The highest OA conversion were obtained after only 15 minutes with

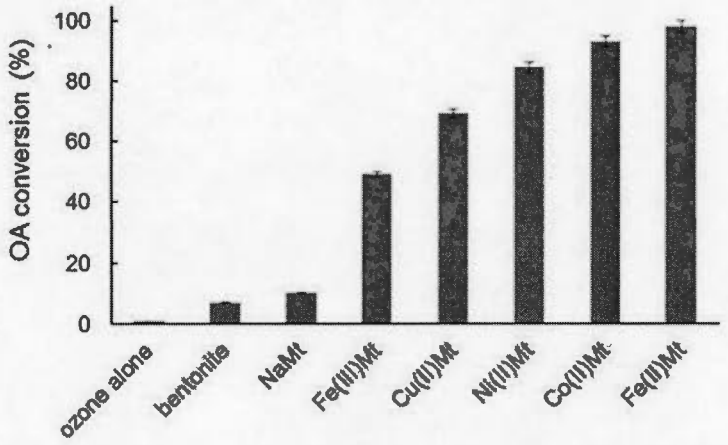


Fig. 3.1. Oxalic acid conversion after 60 min. The initial reaction mixture contained 10^{-3} M OA (±1%) and 2 $g.L^{-1}$ of catalyst (average error ± 0.5 $mg.L^{-1}$) in distilled water, at pH 2.8 ± 2% (intrinsic pH). An ozone stream (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C.

Fe(II)Mt (100%) and Co(II)Mt (95%). Another bentonite used as starting material gave almost similar results (Azzouz *et al.*, 2010).

3.3.2 Effect of catalyst amount

The choice of a 2 g catalyst amount is supported by preliminary investigations on Co(II)Mt, which produced maximum OA conversion of 95-98% after only 15 min. of ozonation at pH 2.8 (Fig. 3.2). Here, each catalyst is expected to act efficiently at a specific optimum amount, which may vary according to the ozonation time and pH.

As a general feature, catalyst pre-swelling in distilled water resulted in higher OA removal yield. In similar conditions, 1.5 g of Co(II)Mt pre-swollen overnight

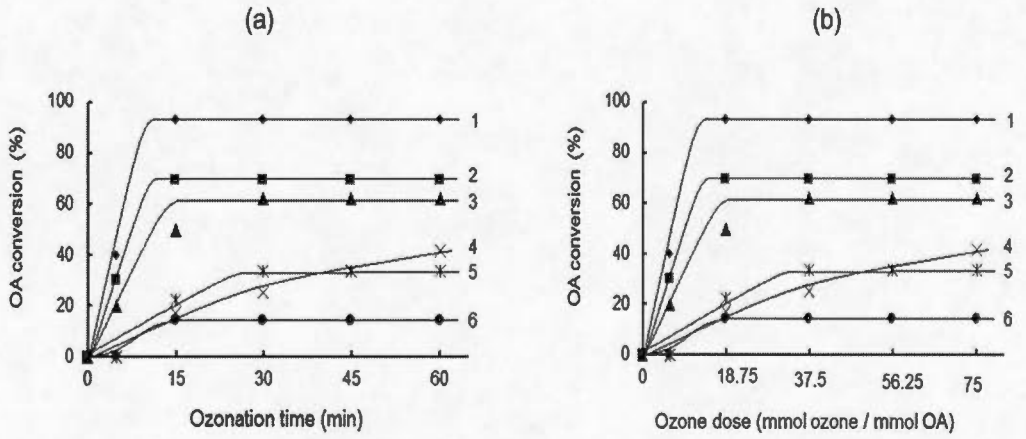


Fig. 3.2. (a) Effect of Co(II)Mt amount on OA conversion at pH 2.8 ± 2%. 1. 2.0 $g.L^{-1}$; 2. 1.5 $g.L^{-1}$; 3. 1.0 $g.L^{-1}$; 4. 0.5 $g.L^{-1}$; 5. 2.5 $g.L^{-1}$; 6. 0.2 $g.L^{-1}$. Initial OA concentration = 10^{-3}M (± 1%). Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C (b) OA conversion in the same conditions as above shown versus ozone dose.

produced ca. 70 % OA decomposition yield after only 15 min., but only 42-43% after at least 30 min. when added as dry powder in the reaction mixture. Therefore, full clay exfoliation by pre-swelling turns out to be an essential requirement for effective ozonation, confirming thereby that adsorption plays a key role in heterogeneous ozonation.

As a common feature, for all fresh catalysts a slight increase in the OA decomposition yield was observed after 1-2 ozonation cycles without regeneration by impregnation in fresh cation solution (Fig. 3.3). This must be due to the disappearance of competitive substrate to oxalic acid in ozonation. In other words,

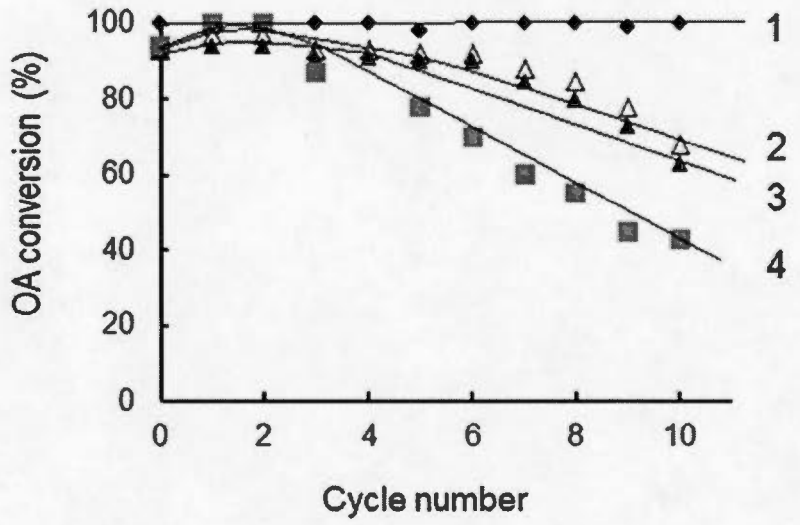


Fig. 3.3. Effect of the re-use cycle number of Fe(II)Mt on OA conversion at pH 2.8 $\pm$ 2%. Initial OA concentration = 10^{-3}M ($\pm$ 1%). Ozone (6 $\pm$ 0.2 mg.min^{-1}) was injected at 25 °C. The sizes of the experimental points accounts for error bars. (1) Regeneration by impregnation in fresh Fe^{2+} solution after each ozonation cycle; (2) Regeneration by calcination at 450 °C in air stream followed by impregnation in fresh Fe^{2+} solution after each ozonation cycle; (3) Regeneration by impregnation in fresh Fe^{2+} solution followed by calcination at 450°C in air stream after each ozonation cycle; (4) Without regeneration

unlike the spent catalyst, uncalcined clay samples still contain organic impurities originating from the native crude bentonite used as raw material for obtained montmorillonite-rich materials.

For higher re-use cycle number, periodical re-impregnation after each in fresh aqueous cation solution use appears to completely revive the catalytic activity, which remains constant at its maximum level up to ca. 50-60 cycles. (Fig. 3.3, curve 1). Without regeneration, the OA conversion dropped dramatically down to 42-45% after ten ozonation cycles using Fe(II)Mt or Co(II)Mt as catalysts (Curve 4). This activity decay was explained in terms of cation loss via partial ion-exchange at pH 2.8, as supported by EDX measurements of the catalyst chemical compositions before and after ozonation. This revealed a decrease of the iron content in Fe(II)Mt with increasing re-use cycle number.

Besides, regeneration by calcination at 450°C in air stream followed by impregnation in fresh Fe^{2+} solution after each ozonation cycle (curve 2) and conversely (curve 3) were found to affect the catalytic activity, producing a decay of the OA conversion. X-ray diffraction analyses revealed a low cristallinity, presumably due to cumulative irreversible dehydroxylation of the catalyst surface, as supported by TG analysis. Thus, one may conclude, that the best and most stable catalysts in time are those previously ozonated for removing the organic impurities, and then periodically regenerated by impregnation in fresh Fe^{2+} solution after each ozonation cycle.

3.3.3 Effect of ozonation time

Deeper insights with 2 $g.L^{-1}$ of each catalyst indicate that the general tendency is that the OA conversion increases in time. A maximum and constant equilibrium value was attained after ca. 15 min. for Fe(II)Mt and Co(II)Mt and ca. 30 min. for less effective catalysts (Fig. 3.4).

In contrast, 2 $g.L^{-1}$ of NaMt showed a conversion not exceeding 7-10% even after 60 min. (Fig. 3.5). Interestingly, a conversion approximately four times higher (40%) was obtained with a catalyst amount of only 1 $g.L^{-1}$ at the same pH (2.8). This amount seems to be optimum, since the OA conversion rose up to its maximum level of 70-75% at pH 3.5 (Fig. 3.6).

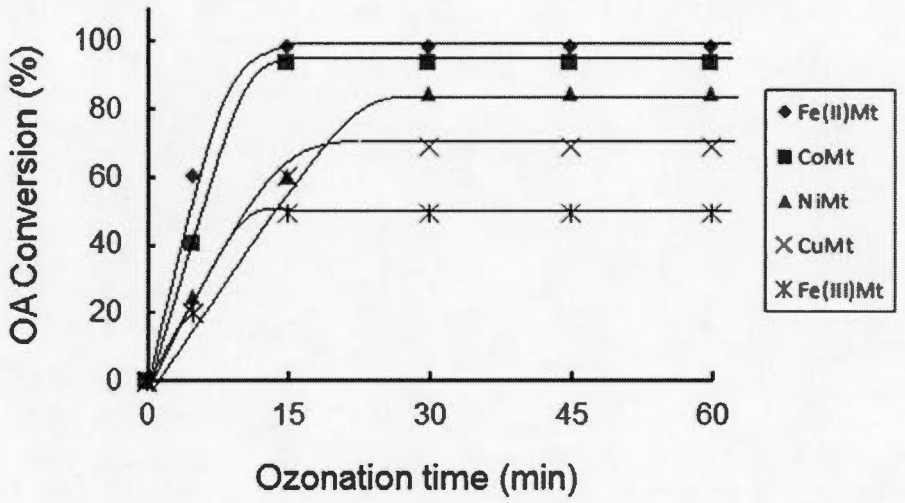


Fig. 3.4. Evolution in time of oxalic acid conversion. The initial reaction mixture contained 10^{-3} M (±1%) OA and 2 $g.L^{-1}$ of catalyst (± 0.5 $mg.L^{-1}$) in distilled water, at pH 2.8 ± 2% (intrinsic pH). An ozone stream (6 ± 0.2 $mg.min^{-1}$) was injected at T= 25 °C. The sizes of the experimental points accounts for error bars.

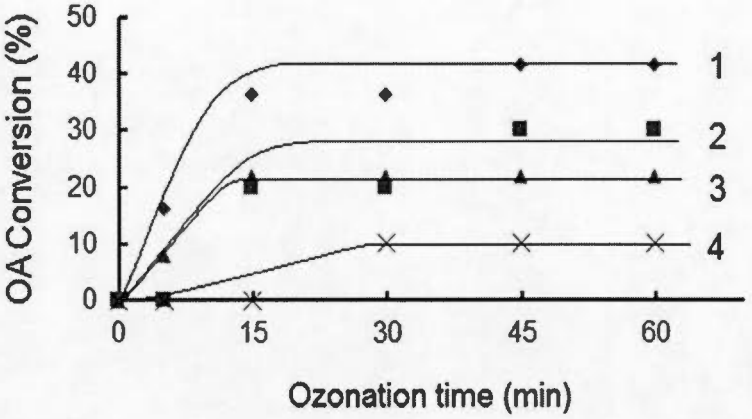


Fig. 3.5. Effect of NaMt amount on OA conversion at pH 2.8 ± 2%. 1. 1.0 $g.L^{-1}$; 2. 0.5 $g.L^{-1}$; 3. 1.5 $g.L^{-1}$; 4. 2.0 $g.L^{-1}$. Initial OA concentration = 10^{-3}M (±1%). Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C. The sizes of the experimental points accounts for error bars.

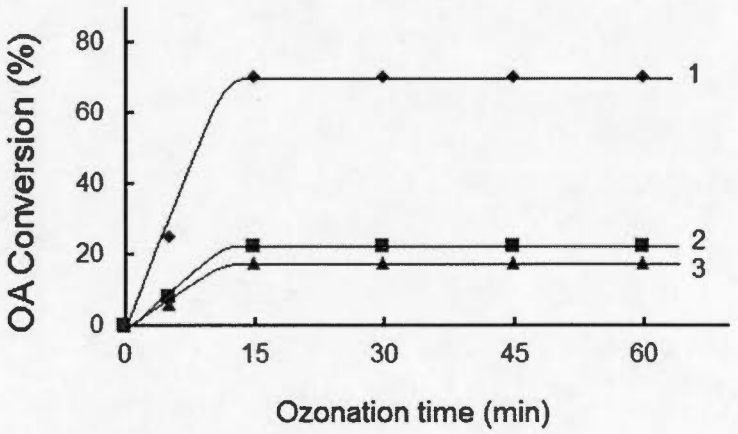


Fig. 3.6. Effect of NaMt amount on OA conversion at pH 3.5 ± 2%. 1. 1.0 $g.L^{-1}$; 2. 1.5 $g.L^{-1}$; 3. 2.0 $g.L^{-1}$ (± 0.5 $mg.L^{-1}$). The sizes of the experimental points accounts for error bars.

This appears to be a common feature of all the catalysts tested, suggesting a strong interaction between the catalyst amount and pH. In other words, pH fluctuations are expected to influence the catalyst activity and conversely. Clear evidence in this regard was provided by the fact that the attenuation of ozonation in time is unavoidably accompanied by an increase in the pH of the reaction mixture. This is most likely due to the progressive formation of weaker acidic species such as CO_2 at the expense of oxalic acid.

3.3.4 Effect of pH

Higher pH values were detrimental for all catalysts, but beyond neutral pH, ozonation was found to weakly reactivate again. After an ozonation time of 60 min. in the presence of Co(II)Mt, the OA conversion dramatically decreased from 95-98% to ca. 30% by increasing pH from 2.8 up to 6.5 (Fig. 3.7). This decay in the catalytic activity is more accentuated for shorter ozonation time (15 min.), since the OA conversion dropped from ca. 98% to approximately 18%.

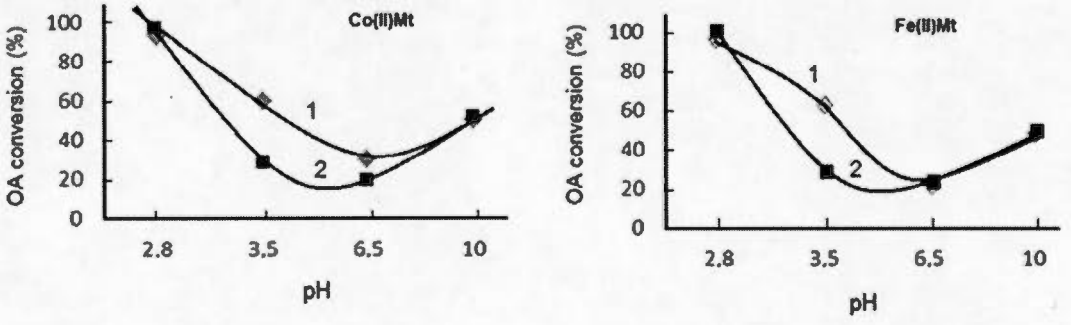


Fig. 3.7. pH effect on the OA conversion for Co(II)Mt at different ozonation times. 1. after 60 min.; 2. after 15 min. The sizes of the experimental points accounts for error bars.

A similar tendency was observed for Fe(II)Mt with decrease in the OA conversion from 98-100% to ca. 20% and 22% for ozonation times of 15 and 60 min., respectively (Fig. 3.7). The critical pH corresponding to the lowest catalytic activity seems to shift to slightly lower values, i.e. from 6.0-6.5 (for 60 min.) to 4.0-4.5 for shorter ozonation time (15 min.). This indicates the occurrence of at least a binary interaction between the ozonation time and pH.

For both Co(II)Mt and Fe(II)Mt, acidic pH (2.8-3.0) produced higher OA conversion (60-100%) even after only 15 min. of ozonation, as compared to higher pH. This result is of great importance, because it opens new prospects to fast ozonation for total mineralization of organic pollutants without pH adjustment of the released waste-waters. This beneficial effect of acidic media is supposed to involve both molecular ozone and surface bound oxygen as oxidizing agents (Nawrocki and Kasprzyk-Hordern, 2010; Yong *et al.*, 2005). Thus, adsorption is expected to play a key-role in the OA ozonation in the presence of solid catalysts.

3.3.5 Effect of temperature

Increasing temperature from 10 to 25°C induced a significant improvement of the OA conversion, e.g. from ca. 15% to approximately 92-95% for Co(II)Mt (Fig. 3.8). This is presumably due to a thermal activation of the ozonation reactions (Daud *et al.*, 2010). Except for the first 5 min of ozonation, pronounced temperature increase up to 40°C did not produce any additional improvement, presumably due to a simultaneous decrease in the ozone amount in the reaction mixture.

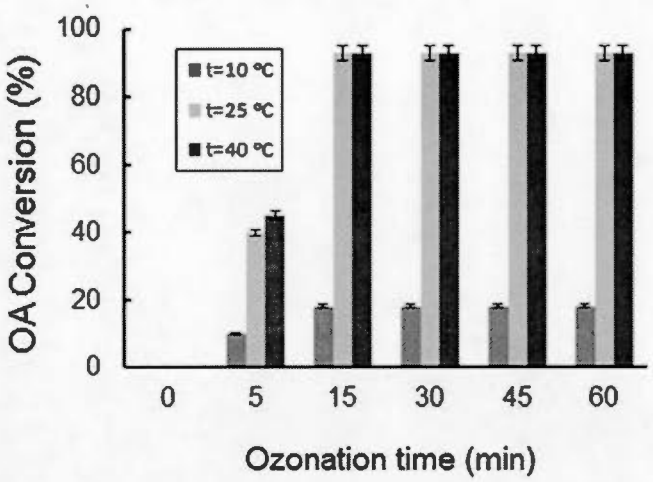


Fig. 3.8. Effect of temperature on the OA conversion for Co(II). Initial OA concentration = 10^{-3} M (±1%); 2 $g.L^{-1}$ of catalyst (± 0.5 $mg.L^{-1}$) in distilled water. Initial pH =2.8 ± 2%. Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C.

The latter must involve a decrease in the ozone solubility in the aqueous media (Huang *et al.*, 2011), but a possible decay in the physical adsorption on the catalyst surface should also be taken into account. Thus, at 25°C, ozonation appears to be optimum, in agreement with other data (Yong *et al.*, 2005; Huang *et al.*, 2011; Sun *et al.*, 2005; Legube and Karpel Vel Leitner, 1999; Huang *et al.*, 2012; Liu *et al.*, 2011). This result is of great importance, because effective ozonation may conveniently be achieved at ambient temperature.

3.3.6 Individual effect assessment

In a second step, deeper insights in the parameter interactions were achieved through 3^3 factorial designs of experiments using the most effective catalysts, namely Co(II)Mt and Fe(II)Mt. For this purpose, 27 ozonation attempts were performed at 25°C for each catalyst, by varying the initial pH of the OA solution (X_1), ozonation

time (X_2), and catalyst amount (X_3), around their apparent optimum values previously assessed (Table 3.1).

Table 3.1. Parameter variation ranges for 3^3 factorial design at T =25°C

Parameter	Symbol (Coded variable)	Variation levels [a]		
		Minimum (−1)	Center (0)	Maximum (+1)
Initial pH	X_1	1.8	2.8	3.8
Ozonation time (min.)	X_2	5	15	25
Catalyst amount ($g.L^{-1}$)	X_3	1	2	3

[a] In brackets: the coded value of the variation levels for expressing the reduced (non-dimensional) value of each parameter.

A quick overview of the measurements of the OA conversion (Y_1) and final pH of the reaction mixture (Y_2) confirmed once again that Fe(II)Mt is slightly more effective than Co(II)Mt (Table 3.2). OA conversion exceeding 40% were obtained with both catalysts (Experiments 11, 13, 14, 16 and 17) at medium initial pH (2.8), which appears to be an optimum value.

Table 3.2. OA conversion (Y_1) and final pH measurements (Y_2) for Co(II)Mt and for Fe(II)Mt

Nr	Reduced parameter level			Co(II)Mt		Fe(II)Mt	
	X_1	X_2	X_3	Y_1	Y_2	Y_1	Y_2
1	-1	-1	-1	0.7	2.03	0.7	2.04
2	-1	-1	0	3.2	2.13	3.9	2.13
3	-1	-1	1	1.8	2.08	1.8	2.07
4	-1	0	-1	1.9	2.09	2.1	2.09
5	-1	0	0	7.9	2.26	8.9	2.27
6	-1	0	1	6.2	2.19	6.2	2.2
7	-1	1	-1	1.9	2.09	2.1	2.09
8	-1	1	0	8.1	2.27	6.2	2.2
9	-1	1	1	6.2	2.19	6.2	2.2
10	0	-1	-1	19.9	3.58	19.9	3.57
11	0	-1	0	40	4.17	60	4.75
12	0	-1	1	2	3.07	7.9	3.24
13	0	0	-1	49.7	4.46	54	4.57
14	0*	0*	0*	93 91 95	5.7 5.6 5.7	98 97 95	5.9 5.9 5.9
15	0	0	1	23	3.67	29.3	3.86
16	0	1	-1	61.2	4.8	63.4	4.85
17	0	1	0	93	5.7	98	5.85
18	0	1	1	34	4.01	41.2	4.21
19	1	-1	-1	5.9	4.56	7.9	4.73

20	1	-1	0	7.9	4.75	19.3	5.74
21	1	-1	1	2.7	4.25	3.41	4.36
22	1	0	-1	13.42	5.28	15.1	5.37
23	1	0	0	25.9	6.48	26.7	6.63
24	1	0	1	7.2	4.69	8.6	4.81
25	1	1	-1	22	6.1	23.86	6.13
26	1	1	0	38.2	7.2	42.1	7.39
27	1	1	1	9.2	4.78	10.2	4.95

*Triplicate measurements of OA conversion and pH at medium parameter levels (experiment 14).

A second condition for decomposing more than 91% of oxalic acid also imposes medium catalyst amounts around 2 g (Experiments 14 and 17). An ozonation time of 15 min. gave comparable OA conversion as 25 min, and turned out to be sufficient to produce effective ozonation. This opens promising prospects for fast and total mineralization of refractory organic pollutants at ambient temperature. As previously stated, in all experiments OA ozonation was unavoidably accompanied by pH increase in the reaction mixture up to neutral, at most. Here, the OA decomposition into CO_2 appears to be proportional to the final pH.

On the basis of the data provided by the 27 experimental attempts, the OA conversion (Y_1) and final pH (Y_2) were modeled for both Co(II)Mt and Fe(II)Mt using a Taylor's second-order polynomial (Bodo *et al.*, 2004; Assaad *et al.*, 2007), as follows:

$$Y_i = a_o + a_1.x_1 + a_2.x_2 + a_3.x_3 + a_{11}.x_1^2 + a_{22}.x_2^2 + a_{33}.x_3^2 + a_{12}.x_1.x_2 + a_{13}.x_1.x_3 + a_{23}.x_2.x_3 + a_{123}.x_1.x_2.x_3$$

Three additional attempts at the central point (0,0,0) allowed estimating the average error in the value of each coefficient, on the basis of the random variance (Table 3.3). Model accuracy was estimated using conventional Student's t-test and Fisher's tests (Assaad *et al.*, 2007). The calculated errors on the coefficient values (Trust range) for Y_1 were of ± 1.13 for Co(II)Mt and ± 1.02 for Fe(II)Mt.

Table 3.3. Adequacy tests and variance analysis for OA conversion (Y_1) and final pH (Y_2) models

Criterion	Symbol/Equation	Co(II)Mt		Fe(II)Mt	
		Y_1	Y_2	Y_1	Y_2
Attempt number	N	27	27	27	27
Attempt number at (0,0,0) point	n	3	3	3	3
Model variance	ν	2	2	2	2
Removal% at (0,0,0) point	y_{01}	93	5.7	98	5.85
	y_{02}	91.3	5.66	97	5.85
	y_{03}	95	5.71	95	5.86
Average yield at (0,0,0) point	$y_0 = \Sigma y_{0i}/3$	93.1	5.69	96.67	5.853
Random variance	$S^2 = \Sigma[y_{0i} - y_0]^2/\nu$	3.43	0.0007	2.33	0.00005
Square root of variance	S	1.85	0.026	1.53	0.0071
Risk factor (chosen arbitrary)	α [a]	0.05 [a]	0.05 [a]	0.05 [a]	0.05 [a]
Student's *t* test factor	$t_{\nu,1-\alpha/2}$	4.3 [b]	4.3 [b]	4.3 [b]	4.3 [b]
Average error on the coefficient value (trust range)	$\Delta a_i = \pm t_{\nu,1-\alpha/2} \times (S/N)^{0.5}$	±1.13	±0.13	± 1.02	± 0.07
Number of remaining coefficients [c]	R	11	10	11	11
Average yield for 27 attempts	$Y_m = \Sigma Y_i/27$	21.71	3.95	24.7	4.08
Residual variance	$S_r^2 = \Sigma(y_i - Y_m)^2/(N-R)$	4289.68	3.71	1275.7	4.39

Degrees of freedom	ν_1	3	3	3	3
Residual degrees of freedom	ν_2	4	4	4	4
Fisher's test	$F=S_r^2/S^2$	1250.64	5300	547.5	87800
Fisher–Snedecor law	$F_{\alpha,\nu1,\nu2}$ [d] $= F_{0.95,3,4}$	6.6 [d]	6.6 [d]	6.6 [d]	6.6 [d]

[a] $\alpha=0.05$ was arbitrarily chosen. In this case, a 95% confidence limit was assumed to be satisfactory.
[b] Student'st test with 2 degrees of freedom at 95% confidence ($t_{2,0.975}$).
[c] After removing the less significant coefficients.
[d] See Fisher–Snedecor tables.

The values calculated for the initial pH were of ± 0.13 and ± 0.07, respectively. From the Student's t-test, it appears that $|a_i| < |\Delta a_i|$ for only two coefficients, namely a_{23} and a_{123}. This is a precise index of the high accuracy level of the experimental measurements. Thus, both coefficients can be eliminated from the model Y_2 for Co(II)Mt, because their corresponding effects are shaded by their respective trust range. According to Fisher's test with a 95% confidence, the fact that $F >> F_{0.95,3,4}$ indicates that the final mathematical models for the OA conversion (Y_1) and initial pH (Y_2) for both catalysts are valid within the parameter variation ranges considered (Table 3.4).

Table 3.4. Model coefficients for OA conversion (Y_1) and final pH (Y_2).

Terms in the polynomial model	Corresponding coefficient in the model					Coefficient role	Effect strength and direction
	Symbol	Co(II)Mt		Fe(II)Mt			
		Y_1	Y_2	Y_1	Y_2		
x_0	a_0	63.4	5.1	71	5.31	Dummy variable	-
x_1	a_1	5.3	1.6	6.6	1.7	Individual effect	Favorable
x_2	a_2	10.5	0.5	9.4	0.4		Strongly favorable
x_3	a_3	-4.7	-0.2	-4.1	-0.2		Detrimental
x_1^2	a_{11}	-36.7	-0.6	-41.6	-0.7	Response-surface convexity (Quadratic terms)	Accentuated maximum
x_2^2	a_{22}	-5.5	-0.2	-4.4	-0.2		Flattened maximum
x_3^2	a_{33}	-20.3	-0.9	-23.5	-1.0		Accentuated maximum
$x_1.x_2$	a_{12}	3.5	0.4	3.1	0.3	Binary interaction	Favorable
$x_1.x_3$	a_{13}	-2.7	-0.2	-2.8	-0.2		Detrimental
$x_2.x_3$	a_{23}	-1.3	-0.1	-1.4	-0.1		Weakly detrimental
$x_1.x_2.x_3$	a_{123}	-1.6	-0.1	-1.5	-0.1	Ternary interaction	Weakly detrimental

The very close values of the model coefficients suggest almost similar behavior for both catalysts in ozonation. The individual effect strength expressed in terms of absolute values of the coefficients of the first order terms vary in the following sequence $a_2 > a_1 > a_3$. The reaction time appears to exert on the OA conversion (Y_1) an individual effect (10.5 for Co(II)Mt and 9.5 for Fe(II)Mt) ca. twice higher than those of pH (5.3 and 6.6, respectively) and the catalyst amount (4.7 and 4.7, respectively). It results that slight increases in the ozonation time within the investigated range induce a significant improvement of the OA conversion, more particularly for medium values of the initial pH. This suggests a strong interaction between these two parameters.

The signs of these coefficients indicate that unlike the catalyst amount (a_3), the ozonation time and, to a lesser extent, pH exerts favorable effects (a_2 and a_1) on Y_1 and Y_2 for both catalysts. Here, high catalyst amounts are supposed to enhance clay-clay interactions at the expense of those involving ozone and (or) oxalate adsorption on the solid surface. This should result in low clay exfoliation and even coagulation-flocculation of the clay mineral, which are expected to reduce the contribution of adsorption more particularly at high pH and prolonged time (Azzouz *et al.*, 2010).

The fact that the initial pH exerts the strongest effect on the final alkalinity suggests that beyond a certain level increasing pH rather contributes in increasing the amount of OH^- ions in the ozonation mixture instead of intensifying the ozonation process. This is supported by the negative impact on the OA conversion for excessive initial pH, which suggests the occurrence of optimum value, around which pH interactions should be more significant than the individual effect.

3.3.7 Assessment of parameter interactions

The ozonation time and initial pH displayed the most significant interaction expressed through the second order terms of the polynomial models for the OA conversion (a_{12}=3.5 for Co(II)Mt and 3.1 for Fe(II)Mt). This indicates an appreciable synergy of these two parameters when increased simultaneously. The two other interactions (-2.7 and -1.3 for Co(II)Mt and -2.8 and -1.4 for Fe(II)Mt) appears to be weaker and detrimental, and must be due to the occurrence of an optimum catalyst amount. Excessive catalyst amount should induce clay compaction, reducing the available surface for adsorption and/or ozone decomposition. The latter appear to be an essential requirement, because of the low intrinsic oxidizing capacity of ozone alone (Azzouz *et al.*, 2010; Büchel *et al.*, 2001). Ozonation is significantly enhanced in the presence of clay catalysts, which is supposed to act at least as surface concentrator of oxalic acid and/or ozone. Ozone adsorption, if any, must strongly depends on pH, and is supposed to occur on weaker Lewis acid sites, as compared to its decomposition into reactive oxidizing species (Alejandro *et al.*, 2011; Chao *et al.*, 2007; Monneyron *et al.*, 2003; Bulanin *et al.*, 1995). Subsequently, effective ozonation requires increasing number of Lewis acid sites, which are electron pair acceptor groups, mainly associated with edge sites or metal cations on Mt. Ozone should act as a fairly strong Lewis base, owing to a high electron density on one of its oxygen atoms due to its resonance structure. This confers to ozone sufficient affinity towards certain solid surfaces (Kasprzyk-Hordern *et al.*, 2003). This affinity should be governed by acid-base equilibria, in agreement with the key roles of pH effect and interactions with the two other parameters.

Ozone adsorption as atomic oxygen, if any, is expected to induce a progressive deactivation of the Lewis sites, which can be readily regenerated by reacting with molecular ozone (Azzouz, 2012; Radhakrishnan and Oyama, 2001; Radhakrishnan *et*

al., 2001; Li and Oyama, 1998). On high number of strong Lewis sites, unadsorbed ozone may be directly decompose into atomic oxygen and peroxide ions without previous adsorption (Bulanin *et al.*, 1995). In both cases, ozone diffusion towards the surface should be an ozonation controlling step, while the availability of high number of Lewis sites is expected to intensify ozone-catalyst interactions (Li and Oyama, 1998). This explains somehow the interactions of the ozonation time with pH and, to a lesser extent, with the catalyst amount.

The pH interaction with the catalyst amount is explained by the formation of oxalate-cation-Mt complexes (OCMC) (Azzouz, 2012). This involves cation bridging effect between the negatively charged clay surface and $HC_2O_4^-$ anion resulting from oxalic acid dissociation (pK_{a1} = 1.27 and pK_{a2} = 4.27) in the investigated pH range. Such a pathway requires high number of accessible surface cation, i.e. not only optimum pH and catalyst amount but also optimum interaction between both parameter. Low catalyst amount and pH below the critical coagulation concentration (CCC) favor clay exfoliation and dispersion, along with adsorption of ozone and oxalic acid, as already reported (Yunzheng *et al.*, 2003; Beltran *et al.*, 2005). This is due to an accentuation of the density of positive charges on Mt and a protonation of the silanol and aluminol terminal groups, which enhance coulombic attraction upon ozone molecules. Nonetheless, this also promotes cation release by ion exchange, and reduces the amount of oxalate anions. Moderate pH increase should attenuate this drawback, but simultaneous increase of the catalyst amount is known to enhance clay-to-clay interactions at the expense of heterogeneous catalysis, explaining thereby the negative sign of the pH-catalyst amount interactions.

3.3.8 Ozone action optimization

As expected, the initial pH and catalyst amount showed relatively higher values of the quadratic terms (a_{11} and a_{33}) as compared to the ozonation time (a_{22}). This indicates accentuated convexity for the corresponding response-surfaces, and predicts precise optimum values of initial pH and catalyst amount, in agreement with our previous statement (Fig. 3.9-3.11).

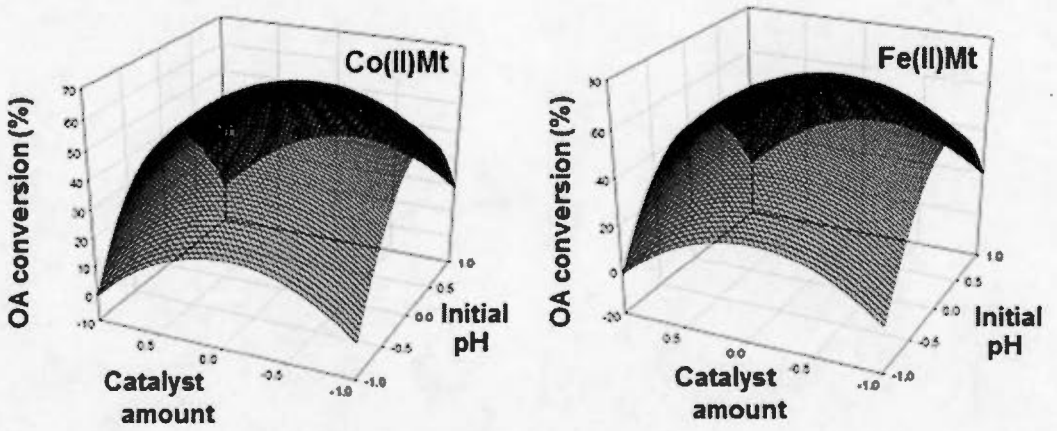


Fig. 3.9. Response-surface of OA conversion for X_2=0 (15 min.). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 mg.min^{-1}) was injected at 25 °C. The catalyst amount and initial pH are expressed in non-dimensional units in the range [-1,1].

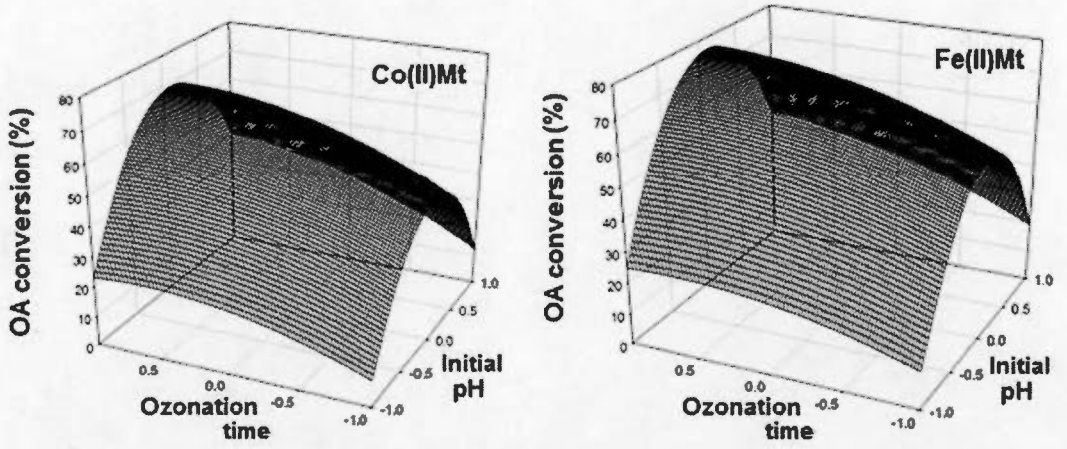


Fig. 3.10. Response surface of OA conversion for X_3=0 (2 $g.L^{-1}$ ± 0.5 mg of catalyst). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C. The ozonation time and initial pH are expressed in non-dimensional units in the range [-1,1].

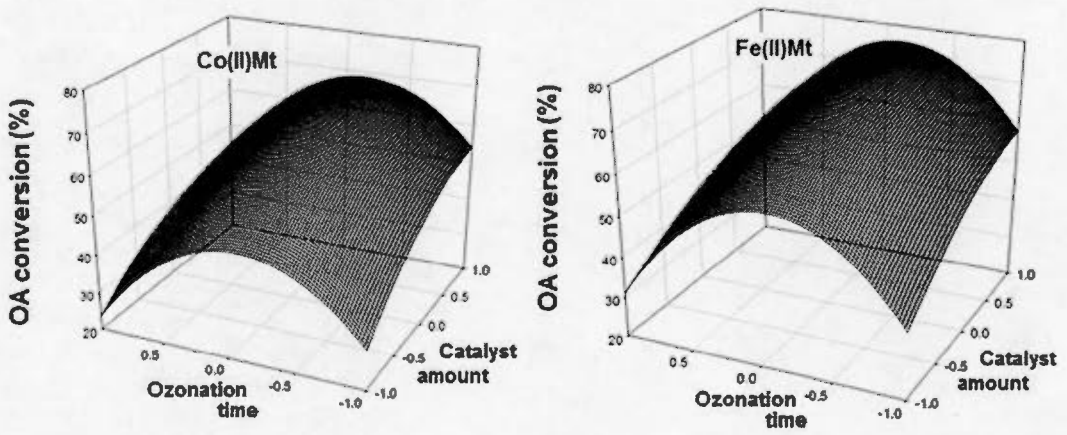


Fig. 3.11. Response surface of OA conversion for X_1=0 (pH 2.8 ± 2%). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C. The ozonation time and catalyst amount are expressed in non-dimensional units in the range [-1,1].

Much less accentuated convexity was obtained for the response-surface describing the final pH of the reaction mixture for both catalysts (Fig. 3.12-3.13). The most significant quadratic term is a_{33}, indicating the occurrence of an optimum value of the catalyst amount (Fig. 3.14).

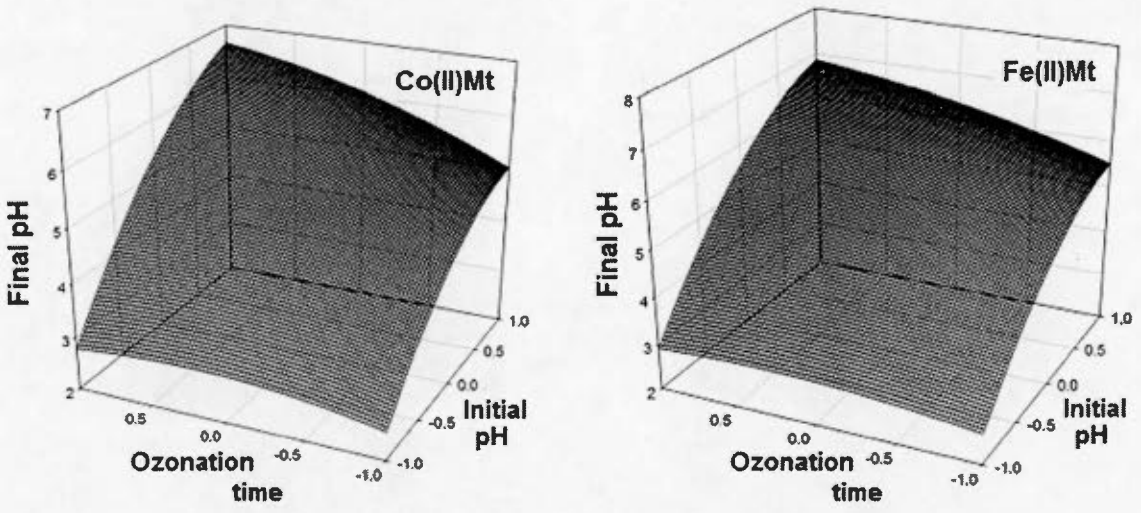


Fig. 3.12. Response surface of final pH for X_3=0 (2 $g.L^{-1}$ of catalyst). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 $mg.min^{-1}$) was injected at 25 °C. The ozonation time and initial pH are expressed in non-dimensional units in the range [-1,1].

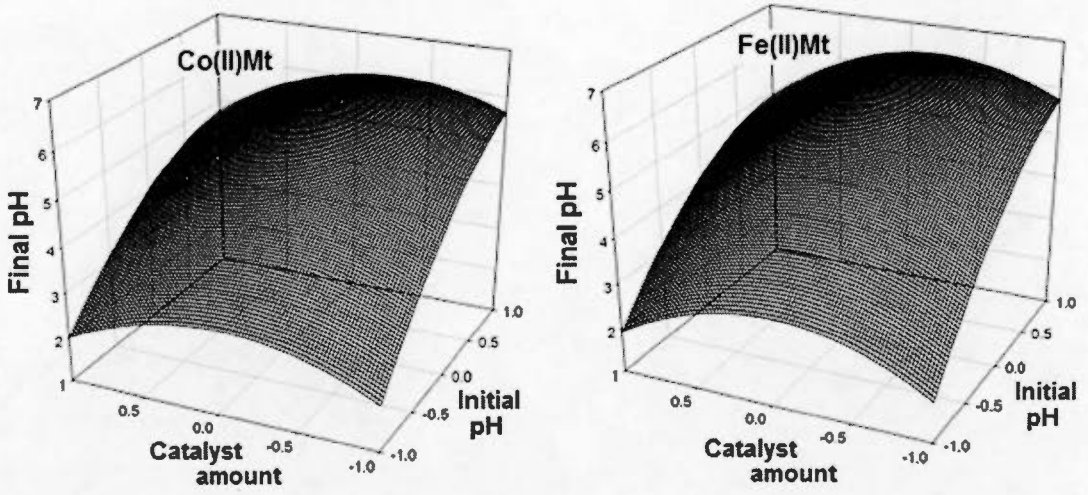


Fig. 3.13. Response surface of final pH for X_2=0 (15 min.). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 mg.min^{-1}) was injected at 25 °C. The catalyst amount and initial pH are expressed in non-dimensional units in the range [-1,1].

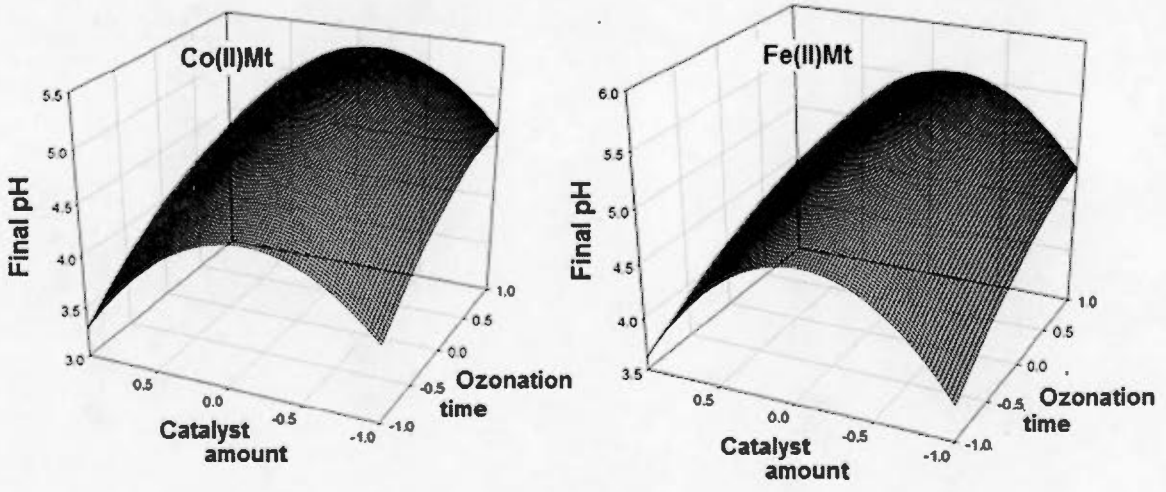


Fig. 3.14. Response surface of final pH for X_1=0 (pH 2.8). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 mg.min^{-1}) was injected at 25 °C. The catalyst amount and ozonation time are expressed in non-dimensional units in the range [-1,1].

Graphical assessment of the optimum parameter values for an ozonation time of 15 min. (X_2=0) showed maximum OA conversion at X_1= 0.068 and X_3= -0.12 for

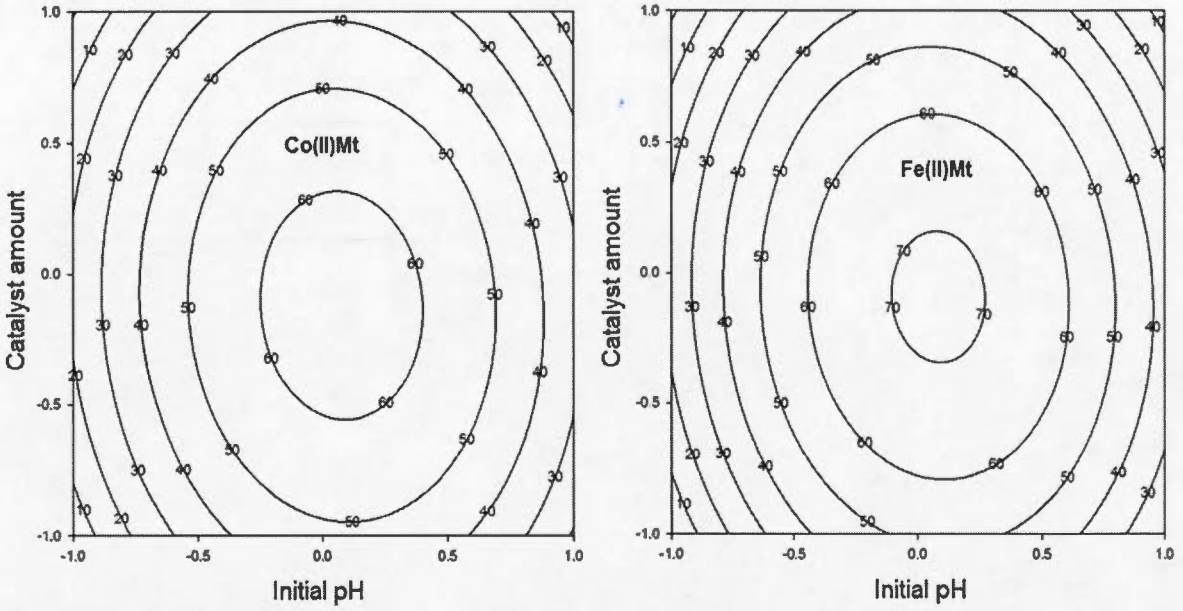


Fig. 3.15. OA conversion versus initial pH (X_1) and catalyst amount (X_3) for X_2=0 (15 min.). Initial OA concentration = 10^{-3} M (±1%); Ozone (6 ± 0.2 mg.min^{-1}) was injected at 25 °C. The catalyst amount and initial pH are expressed in non-dimensional units in the range [-1,1].

Co(II)Mt, and X_1= 0.08 and X_3= -0.09 for Fe(II)Mt (Fig. 3.15). These data are in good accordance with those calculated from the respective mathematical models, and correspond to pH 2.87 and a catalyst amount of 1.88 g.L^{-1} for Co(II)Mt, and to pH 2.88 and 1.91 g.L^{-1} for Fe(II)Mt.

Ozonation triplicate tests at these optimum conditions resulted in total disappearance of oxalic acid within 15 min. with each catalyst. The occurrence of optimum parameters within the variation ranges investigated arises from the judicious choice of the three variation levels for each parameter. Accurate COD and pH measurements provided adequate mathematical models that correlate satisfactorily with the evolution of the OA conversion and final pH in the vicinity of the optimum

conditions. Thus, taking into account the parameters interactions, Co(II)Mt and Fe(II)Mt catalysts require up to 90 mg ozone (1.88 mmol ozone) for decomposing 1 mmol oxalic acid. This result could be improved with higher specific surface area. Investigations are still in progress in this regard.

3.4 Conclusion

The results obtained demonstrate that the use of montmorillonite is an essential requirement to achieved high decomposition yields of oxalic acid via ozonation in water at ambient temperature. The role of montmorillonite must involve not only the catalytic effect of the exchangeable cation but also the contribution of adsorption on the clay mineral surface. Evidence of the role of adsorption was provided by the detrimental effect of increasing temperature, as supported by the decrease in the ozonation yield upon heating. Co(II) and Fe(II) exchanged montmorillonites turned out to be effective catalyst in the ozonation of oxalic acid, affording up to 98 and 100% OA conversion, respectively, after only 15 min. The initial pH and catalyst amount showed significant individual effects and interaction. Total removal of oxalic acid was achieved at pH 2.87 with 1.88 $g.L^{-1}$ of Co(II)Mt, or at pH 2.88 with 1.91 $g.L^{-1}$ of Fe(II)Mt. At this pH level, ozonation is supposed to proceed preponderantly via heterogeneous catalysis, but the homogenous pathway must also take place because of the occurrence of free metal cations resulting from partial ion-exchange. The detrimental effect of increasing pH and catalyst amounts must be due to clay compaction, which is assumed to hinder the cation mobility and adsorption contribution. The synergistic interaction of the initial pH with the other parameters can be explained in terms of enhancing adsorption of oxalate anion and ozone at the expense of the bulk ozonation reaction. Because oxalic acid turned out to be a bottleneck in most oxidation methods, total mineralization of any hazardous organic

pollutants from aqueous media may be envisaged in similar optimum conditions. This opens promising prospects for a low cost and convenient water treatment at ambient temperature, without residual traces of hazardous derivatives.

REFERENCES

Alejandro, S., Valdés, H. and Zaror, C.-A. (2011). Natural Zeolite Reactivity Towards Ozone: The Role of Acid Surface Sites. *Journal of Advanced Oxidation Technologies,* 14, 182-189.

American Society for Testing and Materials. (1976). Annual Book of ASTM Standards. 31-Water, Standard D 1252-67 (p. 473) West Conshohocken: ASTM International.

Assaad, E., Azzouz, A., Nistor, D., Ursu, A.-V., Sajin, T., Miron, D.-N., Monette, F., Niquette, P. and Hausler, R. (2007). Metal removal through synergic coagulation–flocculation using an optimized chitosan–montmorillonite system. *Applied Clay Science*, 37, 258–274.

Azzouz, A. (2012). Advances in Oxidative Decomposition of Oxalic Acid in Aqueous Media, in: J. C. Taylor (Eds.), Advances in Chemistry Research (p. 1 – 31). New York :Nova-Publishers.

Azzouz, A., Kotbi, A., Niquette, P., Sajin, T., Ursu, A.-V., Rami, A., Monette, F. and Hausler, R. (2010). Ozonation of oxalic acid catalyzed by ion-exchanged montmorillonite in moderately acidic media. *Reaction Kinetics Mechanisms and catalysis*, 99, 289 – 302.

Beltran, F.-J. Rivas, F.-J. and Montero-de-Espinosa, R. (2002). Catalytic ozonation of oxalic acid in an aqueous TiO_2 slurry reactor. *Applied Catalysis B: Environmental,* 39, 221-231.

Beltran, F.J., Rivas, F.J. and Gimeno, O. (2005). Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water. *Journal of Chemical Technology and biotechnology*, 80, 973–984.

Beltran, F.-J., Rivas, F.-J. and Montero-de-Espinosa, R. (2005). Iron type catalysts for the ozonation of oxalic acid in water. *Water Research*, 39, 3553–3564.

Beltran, F.-J., Rivas, F.-J., Fernandez, L.-A., Alvarez, P.-M. and Montero-de-Espinosa, R. (2002). Kinetics of Catalytic Ozonation of Oxalic Acid in Water with Activated Carbon. *Industrial & Engineering Chemistry Research,* 41, 6510–6517.

Bhattacharyya, D., Van Dierdonck, T.-F., West, S.-D. and Freshour, A.-R. (1995). Two-phase ozonation of chlorinated organics. *Journal of Hazardous Matererials,* 41, 73-93.

Bodo, R., Ahmanache, K., Hausler, R. and Azzouz, A. (2004). Optimized extraction of total proteic mass from water hyacinth dry leaves. *Journal of Environmental Engineering and Science,* 3, 529–536.

Büchel, G., Denoyel, R., Llewellyn, P.-L. and Rouquerol, J. (2001). In situ surfactant removal from MCM-type mesostructures by ozone treatment. *Journal of Materials Chemistry,* 11, 589-293.

Bulanin, K.-M., Lavalley, J.-C. and Tsyganenko, A.-A. (1995). IR spectra of adsorbed ozone. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 101, 153-158.

Chao, C.-Y.-H., Kwong, C.-W., Hui, K.-S. (2007). Potential use of a combined ozone and zeolite system for gaseous toluene elimination. *Journal of Hazardous Matererials,* 143, 118-127.

Chatterjee, D., Dasgupta, S., Dhodapkar,R.-S. and Raob, N.-N. (2006). Simultaneous degradation of non-emissive and emissive dyes on visible light illuminated TiO_2 surface. *Journal of Molecular Catalysis A: Chemical,* 260, 264-268.

Chung, H.-H., Jung, J., Yoon, J.-H. and Lee, M.-J. (2002). Catalytic Ozonation of PCE by Clay from Tidal Flat Sediments. *Catalysis Letters*, 78, 77–97.

Daud, N.-K., Ahmad, M.-A. and Hameed, B.-H. (2010). Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe–Montmorillonite K10 catalyst. *Chemical Engineering Journal*, 165, 111–116.

Dubey, A., Rives, V. and Kannan, S. (2002). Catalytic hydroxylation of phenol over ternary hydrotalcites containing Cu, Ni and Al. *Journal of Molecular Catalysis A: Chemical,* 181, 151–160.

Eaton, A.-D. and Franson, M.-A.-H. (1975). Standard Methods for the Examination of Water and Wastewater. 14th Ed. Method 508, (p. 550), APHA-AWWA publication.

Garg, A. and Mishra, A. (2013). Degradation of Organic Pollutants by Wet Air Oxidation Using Nonnoble Metal-Based Catalysts. *Journal of Hazardous, Toxic, and Radioactive Waste*, 17, 89–96.

Giordano, G., Perathoner, S., Centi, G., De Rosa, S., Granato, T., Katovic, A., Siciliano, A., Tagarelli, A. and Tripicchio, F. (2007). Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts. *Catalysis Today* 124, 240–246.

Huang, R., Yan, H., Li, L., Deng, D., Shu, Y. and Zhang, Q. (2011). Catalytic activity of Fe/SBA-15 for ozonation of dimethyl phthalate in aqueous solution. *Applied Catalysis B,* 106, 264– 271.

Huanga, R., Lan, B., Chen, Z., Yan, H., Zhang, Q., bing, J. and Li, L. (2012). Catalytic ozonation of p-chlorobenzoic acid over MCM-41 and Fe loaded MCM-41. *Chemical Engineering Journal*, 180 (2012) 19– 24.

Iurascu, B., Siminiceanu, I., Vione, D., Vicente, M.-A. and Gil, A. (2009). Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite. *Water Research*, 43, 1313–1322.

Jans, U. and Hoigne, J. (1998). Activated Carbon and Carbon Black Catalyzed Transformation of Aqueous Ozone into OH-Radicals. *Ozone: Science and Engineering*, 20, 67–90.

Kaptijn, J.-P. (1997). The eco-clear process. Results from full-scale installations. *Ozone: Science and Engineering*, 19, 297–305.

Kasprzyk-Hordern , B., Ziolek, M. and Nawrocki, J. (2003). Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Applied Catalysis B: Environmental,* 46, 639–669.

Kitsopoulos, K.-P. (1999). Cation exchanged capacity (CEC) of zeolitic volcaniclastic materials: Applicability of the ammonium acetate saturation (AMAS) method. *Clays and Clay Minerals*, 47, 688-696.

Legube, B. and Karpel Vel Leitner, N. (1999). Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catalysis Today,* 53, 61–72.

Li, W. and Oyama, S.-T. (1998). Mechanism of Ozone Decomposition on a Manganese Oxide Catalyst.2. Steady-State and Transient Kinetic Studies. *Journal of the American Chemical Society,* 120, 9047-9052.

Liotta, L.-F., Gruttadauria, M., Di Carlo, G., Perrini, G. and Librando, V. (2009). Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity. *Journal of Hazardous Matererials,* 162, 588–606.

Liu, Z.-Q., Ma, J., Cui, Y.-H., Zhao, L. and Zhang, B.-P. (2011). Factors affecting the catalytic activity of multi-walled carbon nanotube for ozonation of oxalic acid. *Separation and Purification Technology*, 78, 147–153.

Massey, L. (2003). Dietary influences on urinary oxalate and risk of kidney stones. *Frontiers in Bioscience,* 8, 584-594.

Monneyron, P., Mathe, S., Manero, M.-H. and Foussard, J.-N. (2003). Regeneration of High Silica Zeolites via Advanced Oxidation Processes-A Preliminary Study About Adsorbent Reactivity Toward Ozone. *Chemical Engineering Research and Design,* 81, 1193-1198.

Nawrocki, J. and Kasprzyk-Hordern, B. (2010). The efficiency and mechanisms of catalytic ozonation. *Applied Catalysis B,* 99, 27–42.

Nidheesh , P.V. and Gandhimathi, R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination* , 299, 1 – 15.

Northcott, G.-L. and Jones, K.-C. (2003). Validation of Procedures to Quantify Nonextractable Polycyclic Aromatic Hydrocarbon Residues in Soil. *Journal of Environmental Quality*, 32, 571 – 582.

Numata, M., Yarita, T., Aoyagi, Y., Yamazaki, M. and Takatsu, A. (2005). Investigation of saponification for determination of polychlorinated biphenyls in marine sediments. *Chemosphere,* 58, 865–875.

Park, J.-N., Wang, J., Choi, K.-Y, Dong, D.-Y., Hong, S.-I. and Lee, C.-W. (2006). Hydroxylation of phenol with H_2O_2 over Fe^{2+} and/or Co^{2+} ion-exchanged NaY catalyst in the fixed-bed flow reactor. *Journal of Molecular Catalysis A: Chemical,* 247, 73–79.

Perathoner, S. and Centi, G. (2005). Wet hydrogen peroxide catalytic oxidation (WHPCO) of organic waste in agro-food and industrial streams. *Topics in Catalysis*, 33, 207–224.

Pines, D.-S. and Reckhow, D.-A. (2002). Effect of Dissolved Cobalt(II) on the Ozonation of Oxalic Acid. *Environmental Science & Technology,* 36, 4046–4051.

Pinker, B., Henderson, W.-D. (1996). Ozone, UV-light, AOPs Water Treatments (p. 307-318). Amsterdam.

Radhakrishnan, R. and Oyama, S.-T. (2001). Ozone Decomposition over Manganese Oxide Supported on ZrO_2 and TiO_2: A Kinetic Study Using in Situ Laser Raman Spectroscopy. *Journal of Catalysis,* 199, 282-290.

Radhakrishnan, R., Oyama, S.-T., Chen, J.-G. and Asakura, K. (2001). Electron Transfer Effects in Ozone Decomposition on Supported Manganese Oxide. *The Journal of Physical Chemistry B,* 105, 4245-4253.

Ramaswamy, V., Krishnan, M.-S. and Ramaswamy, A.-V. (2002). Immobilization and characterization of copper chlorophthalocyanine on alumina-pillared montmorillonite. *Journal of Molecular Catalysis A: Chemical*, 181, 81–89.

Roy, S., Vashishtha, M. and Saroha, A.-K. (2010). Catalytic wet air oxidation of oxalic acid using platinum catalysts in bubble column reactor: A Review. *Journal of Engineering Science and Technology Review*, 3, 95-107.

Santos, A., Yustos, P., Cordero, T., Gomis, S., Rodriguez, S. and Garcia-Ochoa, F. (2005). Catalytic wet oxidation of phenol on active carbon:stability: phenol conversion and mineralization. *Catalysis Today,* 102-103, 213-218.

Savage, G.P. (2002). Oxalates in human foods. *Proceedings - Nutrition Society of New Zealand,* 27, 4-24.

Savage, G.-P., Mason, S.-L., Vanhanen, L. and Busch, J. (2004). Oxalate content of raw and cooked silverbeet. *Proceedings - Nutrition Society of New Zealand,* 29, 26-30.

Savage, G.-P., Vanhanen, L., Mason, S.-L. and Ross, A.-B. (2000). Effect of Cooking on the Soluble and Insoluble Oxalate Content of Some New Zealand Foods. *Journal of Food Composition and Analysis,* 13, 201-206.

Sun, Z.-Z., Ma, J., Wang, L.-B. and Zhao, L. (2005). Degradation of nitrobenzene in aqueous solution by ozone ceramic honeycomb. *Journal of Environmental Sciences,* 17, 716-721.

Yong, K., Wu, J. and Andrews, S. (2005). Heterogeneous Catalytic Ozonation of Aqueous Reactive Dye. *Ozone: Science and Engineering*, 27, 257–263.

Yunzheng, P., Ernst, M. and Schrotter, J.-C. (2003). Effect of phosphate buffer upon CuO/Al_2O_3 and Cu (II) catalyzed ozonation of oxalic acid solution. *Ozone: Science and Engineering,* 25, 393–397.

Zhu, K.-Z., Liu, C.-B., Ye, X.-K. and Wu, Y. (1998). Catalysis of hydrotalcite-like compounds in liquid phase oxidation: (I) phenol hydroxylation. *Applied Catalysis A,* 168, 365–372.

Zhu, X.-F. and Xu, X.-H. (2004). The mechanism of Fe (III)-catalyzed ozonation of phenol. *Journal of Zhejiang University Science,* 5, 1543–1547.

CHAPTER IV

TOTAL MINERALIZATION OF SULFAMETHOXAZOLE AND AROMATIC POLLUTANTS THROUGH Fe^{2+}-MONTMORILLONITE CATALYZED OZONATION

Abstract

The catalytic activity and selectivity of montmorillonite exchanged with Na^{+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations were comparatively investigated in the ozonation of sulfamethoxazole (SMX). Chlorobenzene, benzoic acid, 4-nitrobenzoic, 3-hydroxybenzaldehyde, 4-nitrophenol, and phenol were used as probe molecules having structural similarity with SMX oxidation intermediates. UV-Vis spectrophometry and chemical oxygen demand (COD) measurements showed that Fe(II)-Mt and to a lesser extent Co(II)-Mt produce total mineralization of all organic substrates in less than 40 min. Combined HPLC-mass spectrometry revealed a reverse proportionality between the degradation time and molecular size of the organic substrates. Oxalic acid was recognized as a common bottleneck in the ozonation of any organic substrates. Ozonation initially obeyed a first order kinetics, but adsorption took place after 3-5 min, inducing changes in the mechanisms pathways. These findings may be useful for tailoring optimum oxidative treatment of waters without accumulation of hazardous derivatives.

4.1 Introduction

Human activities have become major sources of a wide variety of organic pollutants with more or less hazardous effects on health, environment and biodiversity (Beltran *et al.*, 2005; Negrel *et al.*, 2012; Nidheesh and Gandhimathi, 2012; Elsousy *et al.*, 2007; Giordano *et al.*, 2007; Daud *et al.*, 2010; Kjellström *et al.*, 2006). At high concentrations, common organic contaminants can be eliminated by conventional techniques such as adsorption, liquid-liquid extraction, coagulation-flocculation and others, but persistent trace amounts are often released in streams, rivers, and seas. Total removal of organic pollutants requires effective water treatments, and Advanced Oxidation Processes (AOPs) appear as interesting routes for this purpose (Diez, 2010; Ito *et al.*, 1996; Ren *et al.*, 2007; Azzouz, 2012; Wang and Fiessel, 2008; Shahidi *et al.*, 2014). Among these, ozonation and catalytic ozonation are particularly suitable for eco-friendly water treatment that can lead to total mineralization of organic pollutants (Shahidi *et al.*, 2014; Azzouz *et al.*, 2010; Munter *et al.,* 2006; Zhao *et al.*, 2009; Guo *et al.*, 2012).

In this regard, a special interest is devoted to aromatic pollutants. Among these, phenol and chlorobenzene are major intermediates in the manufacture of insect repellents, benzoate plasticizers, cleaning agents, resins, adhesives, alkyde paints, inks, dyestuffs, waxes, polishes, fibers, phenolic resins, bisphenol, rubber, leather tanning agents, ink, dyes, illuminating gases, disinfectants, antiseptics, lotions, perfumes, and intermediates in the production of nylon (Rossberg *et al.*, 2005, p. 112-114). Other aromatic compounds such as 4-Nitrophenol, nitrochlorobenzenes and biphenyl oxides, benzoic acid, 4-nitrobenzoic acid and 3-hydroxybenzaldehyde and their derivatives are also employed in most of the aforementioned applications. A common feature of some aromatic compounds is their use in pharmaceutical industries as active agents against a wide range of microorganisms, antifungal agents

to preserve drugs, and as intermediates in the manufacture of antibiotics and other drugs (Rossberg *et al.*, 2005, p. 112-114; Maki and Takeda, 2005, p. 4-7).

Their antimicrobial activity explains their toxicity for human health and biodiversity. For instance, beyond an acceptable maximum contaminant level (MCL) of 0.1 mg/L or 100 ppb, chlorobenzene is highly harmful for human health (Rossberg *et al.*, 2005, p. 112-114). Benzoic acid and its derivatives may react with vitamin C, giving rise to traces of benzene, known to be a carcinogenic compound (Kasper *et al.*, 2004, p. 618; Smith, 2010). Dermal and oral contact with Ph-CO_2H causes nervousness, nausea, vomiting, constipation, albuminuria, urticaria, asthma, and rhinitis. 4-Nitrobenzoic acid displays antibacterial properties against staphylococci and streptococci infections, and some mutagenic effects against human, with a LD_{50} value of 0.77 g/kg in mice (Booth, 2005, p. 9-11). Chronic contact with 4-nitrobenzoic acid may cause gastrointestinal irritation, cardiac failure, hepatitis, leukopenia and nephritis. Direct contact or inhalation of 3-hydroxybenzaldehyde provokes irritation of the gastrointestinal tract, eyes, skin, and respiratory tract (Bruhne and Wright, 2005, p. 9-10). Exposure to 4-nitrophenol may cause liver and renal dysfunction, headaches, drowsiness, nausea, cyanosis, methemoglobinemia, necrosis of the skin and mucous membranes. It is also assumed to be a tumor promoting agent. 4-Nitrophenol was reported to have a lethal dose (LD_{50}) of 0.4 g/kg in mice (Brecken-Folse *et al.*, 1994). Depending on the concentration, poisoning with phenol may cause insomnia and unconsciousness, upper respiratory tract irritation, severe renal failure, wheezing, headache, nervousness, weight loss, muscle twitching, partial paralysis, etc. (Park, 2010).

The presence of a phenyl ring in aromatic pollutants suggests nearly similar degradation pathways for antibiotics and other drugs via incomplete oxidative treatments or natural oxidation in air under sunlight exposure. This is a major issue to

be tackled because of the presence of drugs and hormone regulators in urban wastewaters. An attempt in this regard resides in correlating the ozonation of a synthetic antibiotic, e.g. sulfamethoxazole (SMX), to that of common aromatic pollutants. SMX is widely prescribed to human and animals for infections such as pneumonia, coccidiosis and gastroenteritis. Only a small SMX part is metabolized, the other part being eliminated by urine. Being present in high concentrations in surface waters and household wastewaters (Rodayan *et al.*, 2010), SMX was ranked in 2007 the sixth most commonly prescribed antibiotic in Canada (Baquero *et al.*, 2008). High levels of residual antibiotics in wastewater may increase the resistance of certain bacteria (Baquero *et al.*, 2008; Dirany *et al.*, 2011). Despite the SMX level allowed by regulatory organizations is limited to 1 ppm (Mar Gómez-Ramos *et al.*, 2011), SMX concentrations of 370 ppm and beyond have been detected in sewages of water-treatment plants.

SMX, like many pharmaceutical products, cannot be easily eliminated by conventional oxidation processes. Its natural degradation by means of biological methods usually gave unsatisfactory results (Dirany *et al.*, 2011; Mar Gómez-Ramos *et al.*, 2011). SMX decomposition barely reaches 32–49% by treating conventional activated sludges (Dirany *et al.*, 2011). Even more oxidative treatments of wastewaters failed in producing total mineralization (Martin de Vidales *et al.*, 2012; Sharma *et al.*, 2006; Dantas *et al.*, 2008; Hu *et al.*, 2007; Beltra *et al.*, 2009; Trovo *et al.*, 2009; Gonzalez *et al.*, 2007; Li *et al.*, 2008; Boudreau *et al.*, 2010), generating sometimes toxic derivatives (Dirany *et al.*, 2011).

We already demonstrated that, in optimum conditions, catalytic ozonation using Fe^{2+}-exchanged montmorillonite produces total mineralization of oxalic acid, which is renowned to be quite refractory to oxidation (Shahidi *et al.*, 2014).This finding has stimulated our investigations to attempt similar treatment under similar operating

conditions to SMX and aromatic pollutants such as chlorobenzene (PhCl), benzoic acid ($PhCO_2H$), 4-nitrobenzoic acid ($p\text{-}O_2N\text{-}PhCO_2H$), 3-hydroxybenzaldehyde (HOPhCHO), 4-nitrophenol ($p\text{-}O_2N\text{-}PhOH$) and phenol (PhOH). The presence of an aromatic ring is expected to involve similar degradation pathways, and help understanding the influence of substituents on the chemical reactivity of persistent intermediates towards ozone. Mass spectrometry identification of the main by-products after incomplete ozonation will certainly provide valuable data for better monitoring the successive steps involved in the total mineralization of each organic molecule investigated herein.

4.2 Experimental

4.2.1. Catalyst preparation and characterization

Fe^{2+}-montmorillonite (Fe(II)-Mt) samples with different iron contents were obtained from bentonite purification into Na+-montmorillonite (NaMt), and impregnation with aqueous $FeCl_2$ solutions for different contact times of 1-7 hours. The iron content of the Fe(II)-Mt catalysts increased from 0% (pure Na-Mt) to 27.3%, 52.5%, 79.5%, and 100% of the cation exchange capacity (CEC), which was assessed by ammonium acetate saturation method (AMAS) and Kjeldahl ammonium distillation technique (Kitsopoulos, 1999). Co(II)-Mt, Ni(II)-Mt and Cu(II)-Mt were prepared via impregnation with their corresponding nitrate metal salt solutions. All catalysts were characterized through X-ray diffraction (XRD, Siemens D5000 instrument, Co-Kα at 1.7890 Å), X-Ray fluorescence (XRF, S-4 Pioneer-Bruker), nitrogen adsorption–desorption isotherm at 77 K (Quantachrome Autosorb equipment), thermal gravimetry (DTG-TG, Seiko TG/TDA6200 device, 120 $ml.min^{-1}$ air stream at $5^{\circ}C.min^{-1}$ scanning rate).

Bentonite purification and full ion-exchange resulted in a perfectly parallel arrangement of the clay sheets, as supported by sharp 001 XRD reflexion reflexion (Fig. S2). The d_{001} basal spacing from 13.1 to 10.3 Å. The Si/Al ratio slightly decreased from 2.575 (bentonite) to 2.519 (NaMt) (Table S1), due to the elimination of denser silica phases such as quartz and cristoballite, as supported by the increase in BET surface area from 50 $m^2.g^{-1}$ (bentonite) to 59 $m^2.g^{-1}$ (NaMt). The latter remained almost constant after exchange with Fe^{2+} cations, because no significant change in the d_{001} basal spacing was noticed, presumably due to compensatory effects of smaller cation radius but higher hydration grade for Fe^{2+} as compared to Na^+ ion. All uncalcined catalysts showed a slight improvement in the catalytic activity after 1–2 ozonation cycles, due to the degradation of organic impurities originating from the parent bentonite. This is supported by TG analysis, which revealed an endo process at 350-450°C assigned to decomposition upon calcination in air stream (Fig. S3). The endo peak at 550-700°C assigned to dehydroxylation was strongly attenuated after repeated calcinations, indicating a partially irreversible loss of structural water, but no change in the catalytic activity was noticed (Appendix B). Higher re-use number beyond 50–60 cycles was found to impose periodic re-impregnation with fresh Fe^{2+} solution for preserving the catalytic activity. This is due to cation loss via partial ion-exchange at pH 2.8 (Shahidi *et al.*, 2014). However, this pH level did not produce any loss in crystallinity.

The surface basicity was assessed by thermal programmed desorption measurements (TPD) of the CO_2 retention capacities (*CRC*) under a 5 $mL.min^{-1}$ nitrogen stream at a 5°C.min^{-1} heating rate between 20 and 400°C, in tubular glass reactor coupled to a Li-840A CO_2/H_2O Gas detector.

4.2.2. Ozonation tests

Ozonation was performed by ozone bubbling (6 $mg.min^{-1}$) produced by an A_2Z ozone generator in a glass reactor containing $3x10^{-4}$ M solutions of phenol, chlorobenzene, benzoic acid, 4-nitrobenzoic acid, 3-hydroxybenzaldehyde, 4-nitrophenol and sulfamethoxazole. One used similar catalyst amount (1.91 $g.L^{-1}$) in powder form (average particle size of 0.1-0.2 mm) and pHs (2.88) as optimized for oxalic acid (Shahidi *et al.*, 2014). When necessary, the initial pH was adjusted using concentrated hydrochloric acid and periodically measured (Accumet 15 pH-meter). After ozonation and catalyst removal by centrifugation, the supernatant was analyzed by UV-Visible spectrophotometry (Cary 1 E instrument) and a standard chemical oxygen demand method (COD) (Eaton and Franson, 1975, p. 550; American Society for Testing and Materials, 1976, p. 473) using a linear calibration curves, like that plotted for phenol taken as the reference (Fig. S4). Almost total COD removal corresponds to a complete mineralization (Appendix C).

4.2.3. Product and intermediate analysis

Liquid Chromatography-Time of Flight-Mass Spectrometry analyses (LC-ToF-MS) were carried out using an Agilent 1200 HPLC system equipped with a binary pump, an in-line degasser, a high performance auto-sampler and a thermostated column division. These analyses were run using a linear gradient of acetonitrile-0.1% HCOOH in H_2O (5-85%, v/v) for 14 min with a flow rate of 0.4 $ml.min^{-1}$ on an Agilent SB-C18 column (2.1×30mm; particle size of 3.5µm), and a column temperature of 25°C. Detailed procedures are provided in the supplementary information file, inspired from some procedures provided by literature (Moheb *et al.*,

2011; Segarra *et al.*, 2006). Appendix D described LC-MS analyses set-up in detail.

4.3 Results and discussion

4.3.1 Effect of catalyst addition

Preliminary ozonation attempts were achieved with SMX and phenol, the simplest probe molecules investigated herein, revealed a significant depletion of the main UV–Vis band at 269 nm by a factor of ca. 90% in the first 10 min of ozonation without catalyst (Fig. 4.1-a). A similar tendency was noticed for sulfamethoxazole (Fig. 4.1-b).

Addition of Fe(II)Mt catalyst produced a total disappearance of this UV bands, as a common feature of all organic substrates investigated herein (Fig. S5). This effect can be better illustrated by the evolution in time of the difference between the relative absorbances before and after catalyst addition, expressed in terms of ($\Delta(A/A_0)$) (Fig. 4.2).

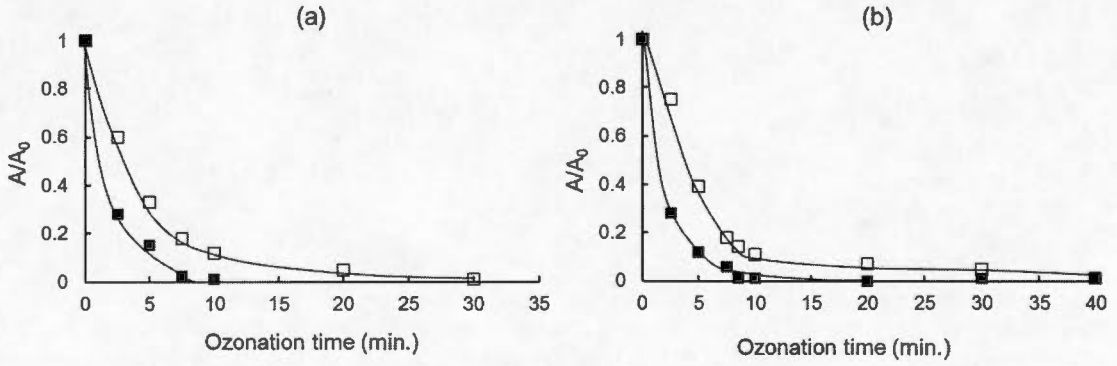


Fig. 4.1. Decay in time of the relative absorbance for phenol at 269 nm (a) and sulfamethoxazole at 266 nm (b); □ ozonation without catalyst; ■ catalytic ozonation. Fe(II)-Mt concentration: 1.91 $g.L^{-1}$; $C_0=3.10^{-4}$ M; initial pH=2.88.

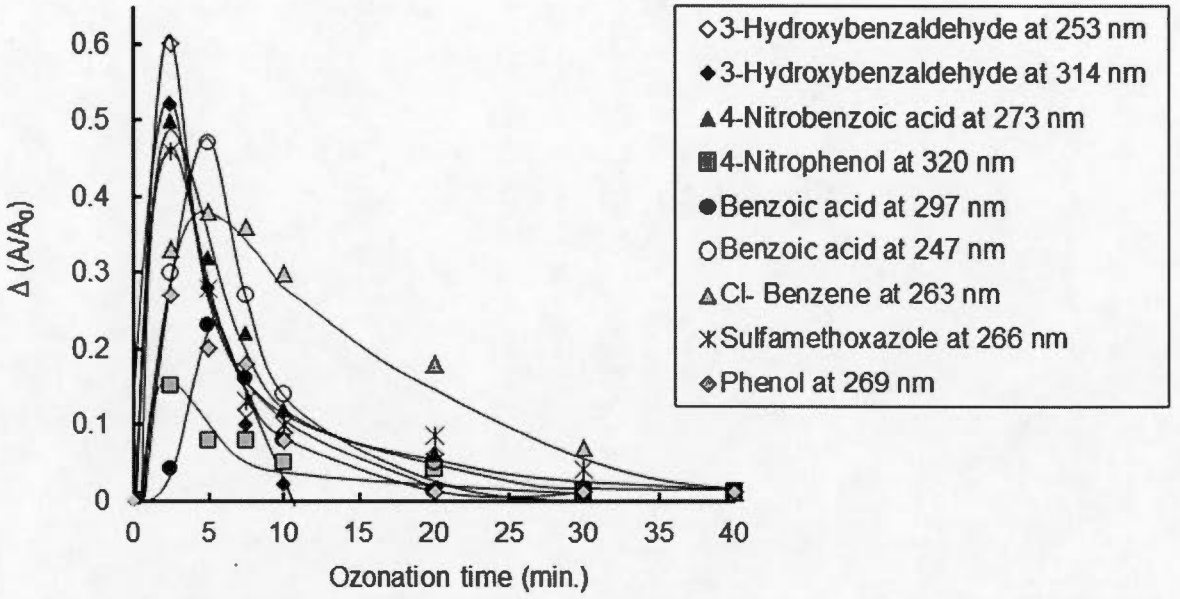


Fig. 4.2. Evolution in time of the decrease in the relative absorbance of the main UV-Vis band; Fe(II)Mt amount: 1.91g.L^{-1}; C_o=3.10^{-4}M; initial pH=2.88.

The highest and fastest catalytic activity of Fe(II)-Mt on the degradation of 3-hydroxybenzaldehyde (both at 253 nm and 314 nm), nitrobenzoic acid (273 nm) and sulfamethoxazole (266 nm) is reflected by the peaks registered after the first 3 min of ozonation. This must be due to, at least, phenyl ring hydroxylation, which appears to be the first step in the ozonation of aromatic compounds. The weakest catalytic effect was noticed for 4-nitrophenol (at 320 nm). Between these two limits, moderate catalytic effects were registered for phenol (at 269 nm) and to a lesser extent, benzoic acid (247 and 297 nm) and chlorobenzene (263 nm), but with slower degradation rate, inasmuch as the activity peak appeared only after 5 min. This is presumably due to their higher oxidation state. Paradoxically, the UV-Vis bands of phenol (269 nm) and benzoic acid (297 nm) totally disappeared after 20 min in the presence of catalyst. Here, one must expect that the presence of highly electrophilic groups such as -NO_2, -CO_2H and –Cl contributes markedly to the stabilization of the phenyl ring.

This finding is of great importance, because it demonstrates that the reactivity towards ozone increases with increasing molecular complexity, but decreases with increasing oxidation states.

The consecutive decrease of $\Delta(A/A_o)$ indicates a quick decay of the catalyst activity, partly due to a pH increase, which is supposed to induce change in the mechanism pathways (Azzouz *et al.*, 2010). An additional explanation involves a temporary catalyst poisoning due the adsorption of base-like intermediates such as hydroquinone (pK_{a1}=9.9), catechol (pK_a=9.48) and resorcinol (pK_a=9.15) and others. This is well supported by total catalyst regeneration through prolonged or repetitive ozonation.

Fe(II)Mt addition induced an appreciable but slower COD decrease, since no total mineralization was achieved in the presence of Fe(II)Mt catalyst even after 20 min ozonation (Fig. 4.3). Almost total COD removal (97%) requires ozonation times of at least 20-40 min for all the organic substrates investigated herein (Fig. S6-curve 1).

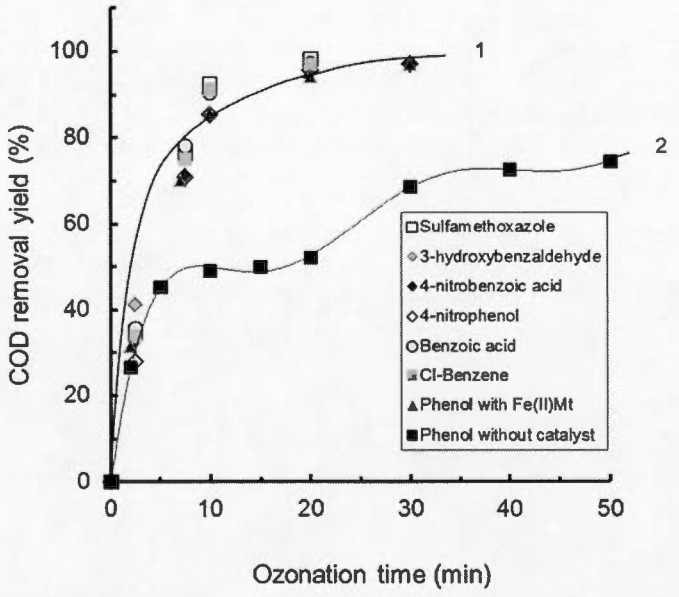


Fig. 4.3. Evolution in time of COD removal yield in the catalyzed ozonation of various $3x10^{-4}$ M substrate solutions (1) as compared to phenol ozonation without catalyst (2). Fe(II)-Mt concentration: 1.91 $g.L^{-1}$; initial pH = 2.88

Total degradation of the organic substrate and complete mineralization into CO_2 were expressed in terms of total disappearance of the UV-Vis band and COD, respectively, required different ozonation times (Table S2). The latter were significantly shortened in the presence of Fe(II)-Mt from more than 100 min to 20-40 min according to the organic substrates.

4.3.2. Changes in pH

The final pH of the reaction mixture increased unavoidably during ozonation, being more pronounced in the presence of Fe(II)-Mt catalyst (Fig. 4.4). The curve shape suggests at least two ozonation steps, with an ozonation time threshold around 10 min, for all organic substrates (Fig. 4.5).

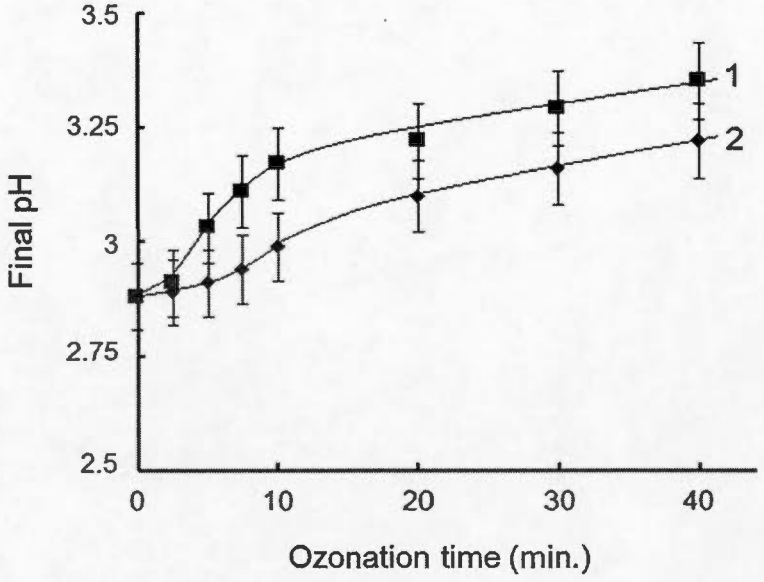


Fig. 4.4. pH evolution in time during phenol ozonation with (1) and without (2) catalyst. Fe(II)-Mt amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88

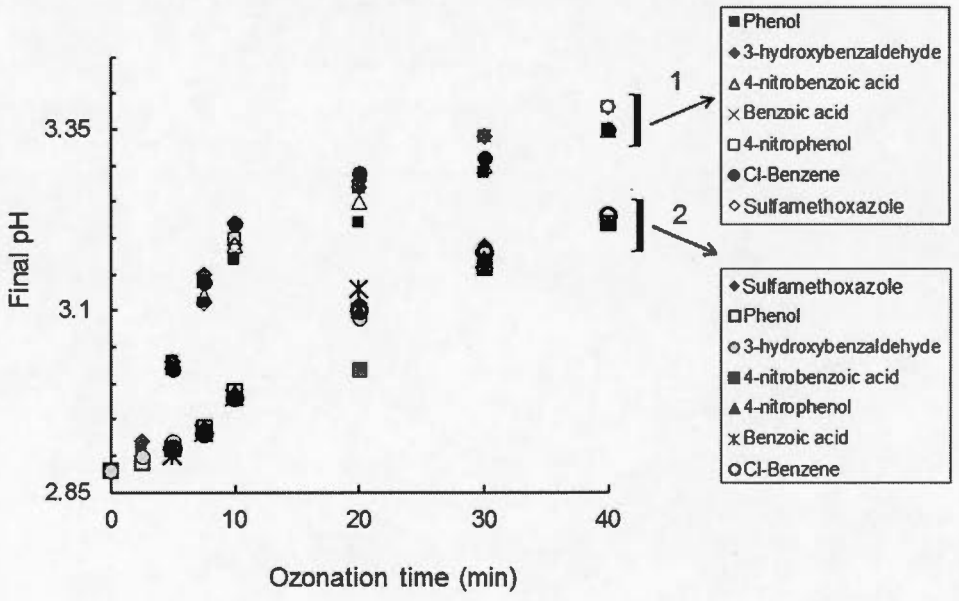


Fig. 4.5. pH evolution in time in the ozonation of different molecules with (1) and without (2) catalyst. Fe(II)Mt amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88

This pH increase must be due to the formation of derivatives with higher pKa. This agrees with our previous explanation in terms of temporary catalyst poisoning by adsorption of amphoteric to alkaline intermediates such as hydroquinone (pK_{a1}=9.9), catechol (pK_a=9.48) and resorcinol (pK_a=9.15) during the first 10 min. After 10 min, pH increase is attenuated, most likely due to the appearance of buffering processes. This can be explained by the formation of weakly acidic derivatives with moderate pKa values, such as muconic (pK_a=3.87), acetic (pK_a=4.75), fumaric (pK_{a1}= 3.03; pK_{a2}= 4.44), maleic (pK_{a1}= 1.83 - pK_{a2}= 6.59), formic (3.751), malonic (pK_{a1}= 2.83, pK_{a2}= 5.69) and oxalic (pK_{a1}= 1.2, pK_{a2} = 4.3) acids. These results are expected to be very useful for investigating the catalytic ozonation of sulfamethoxazole. For this purpose, emphasis was made on the effect of the cation type and content.

4.3.3 Sulfamethoxazole degradation

4.3.3.1 Cation effect

Deeper insights in this regard revealed marked depletion of the relative absorbance at 266 nm and COD till total disappearance after 10 min and 30 min ozonation, respectively (Fig. S7-S8). Shorter ozonation time of 20 min gave COD removal of ca. 98-99% with Fe(II)-Mt catalyst (Fig. 4.6). This performance progressively decreased to 97% for Co(II)-Mt, 95% for Ni(II)-Mt, 92% for Cu(II)-Mt and below 85% for Na-Mt under similar conditions.

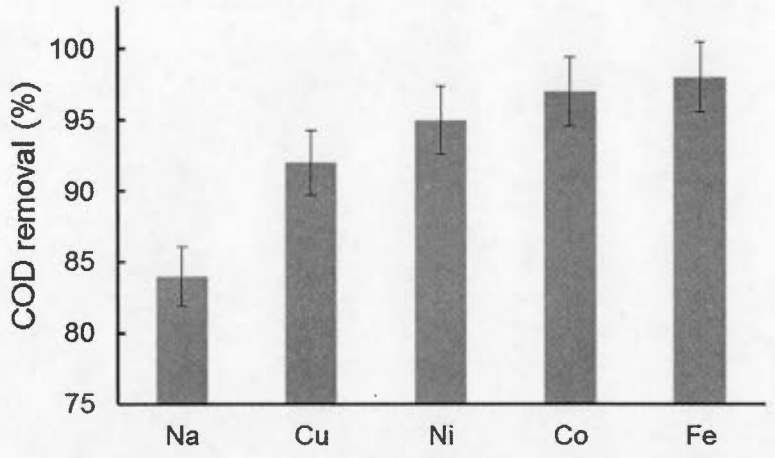


Fig. 4.6. COD removal in sulfamethoxazole ozonation for different Mt-supported cations. Catalyst amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88; ozonation time:20 min.

The required times for total disappearance of the highest UV-Vis band (266 nm) was 8.0, 8.5, 9.5, 9.5, and 20 min. for Fe(II)Mt, Co(II)Mt, Ni(II)Mt, Cu(II)Mt, and NaMt, respectively. The corresponding final pH values were 3.32, 3.31, 3.28, 3.25, and 3.12 respectively. In agreement with previous data (Shahidi *et al.*, 2014; Azzouz *et al.*, 2010), Fe^{2+} and, to a lesser extent, Co^{2+} exhibited the highest catalytic activity for ozonation. Fe^{2+} cation turns out to be the strongest ozone scavenger and OH radical precursor (Azzouz, 2012). Besides, Fe(II)Mt displayed higher acidity-to-basicity ratio (3.81) as compared to Co(II)Mt (2.7) and NaMt (0.23) and to its highest amount of strong acid sites (Table S3). The latter are supposed to favor [Fe^{2+}- organic ligand] associations, which are known to behave as very reactive species towards ozone as complex. Montmoriilonite-supported Fe^{2+} cation can contribute both as free cation released upon ion-exchange in acidic media and as exchangeable cation, which still behaves as a relatively ''free" cation in the vicinity of the clay surface. In other words, Fe(II)Mt promotes ozonation both in the liquid media with and without Fe^{2+} cations, and on the clay surface on the exchangeable site (catalytic effect) and aside between these sites (mainly adsorption).

4.3.3.2 Effect of iron content

Because iron (II) cations shower higher effectiveness in both dispersed and supported forms (Azzouz, 2012; Shahidi *et al.*, 2014; Azzouz *et al.*, 2010), deeper insights in the effect of Fe(II) content were made (Fig. S9-S10). Fully ion exchanged Fe(II)-Mt produced almost total COD removal after 20 min and disappearance of the 266 nm band after 8.5 min (Table S4). COD removal after 20 min of ozonation was found to increase with increasing iron content, but almost total COD removal was also obtained with a minimum ion exchange percent of 79.5% (Fig. 4.7).

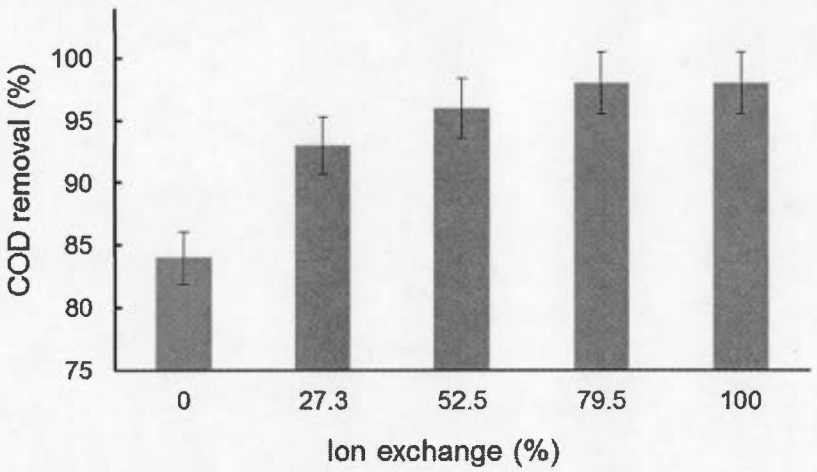


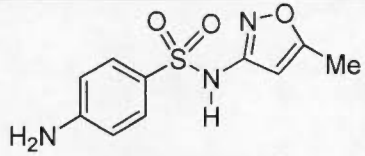
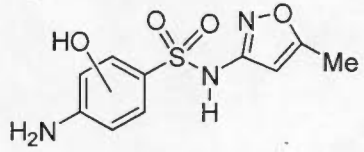
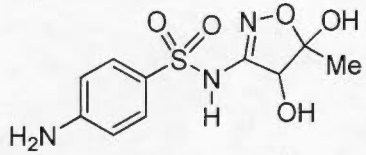
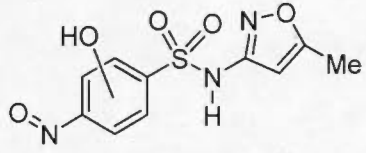
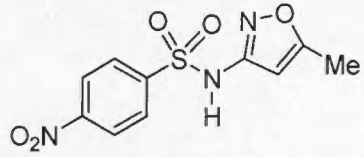
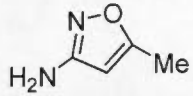
Fig. 4.7. COD removal in sulfamethoxazole ozonation with Fe(II)Mt at different iron contents. Error in Fe content: 3%. Fe(II)Mt amount: 1.91 $g.L^{-1}$; $C_o=3.10^{-4}$ M; initial pH=2.88; ozonation time:20 min.

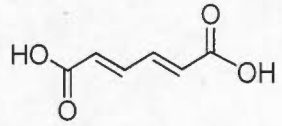
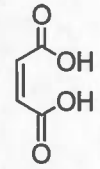
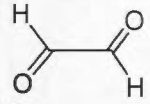
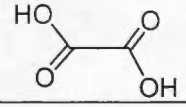
This proportionality between the catalytic activity, expressed in terms of COD removal yield, and the iron (II) content provides clear evidence that the exchangeable Fe^{2+} cation belonging to the clay mineral surface is directly involved in the ozonation process. This ion-exchange threshold must involve optimum ratio between adsorption sites and catalytic centers, which is strongly dependent on the equilibria involving reactant adsorption, desorption and residual intermediate retention, if any.

4.3.3.3 Identification of sulfamethoxazole derivatives

Complete decomposition without total mineralization of the organic substrate results in the formation of intermediates, some of them being regarded as key-intermediate when involved in key-steps. Their identification and quantification through LC-MS (Fig. S11-S16) provided valuable information on the decomposition pathway of the parent compound. The main intermediates identified after sulfamethoxazole ozonation are summarized in Table 4.1.

Table 4.1. Main intermediates in SMX catalytic ozonation.

Compound	Reaction involved	Chemical formula	Structural formula
Sulfamethoxazole	None	$C_{10}H_{11}N_3O_3S$	
Intermediate 1	Phenyl ring hydroxylation	$C_{10}H_{11}N_3O_4S$	
Intermediate 2	isoxazole ring di-hydroxylation	$C_{10}H_{12}N_3O_5S$	
Intermediate 3	Phenyl ring hydroxylation and amino group oxidation	$C_{10}H_9N_3O_5S$	
Intermediate 4	amino group oxidation	$C_{10}H_9N_3O_5S$	
Intermediate 5	isoxazole ring scission	$C_4H_6N_2O$	

Benzoquinone	Phenyl ring scission and oxidation	$C_6H_4O_2$	
Muconic acid	Benzoquinone ring opening and hydroxylation	$C_6H_6O_4$	
Maleic acid	Benzoquinone ring opening and hydroxylation	$C_4H_4O_4$	
Glyoxal	Maleic acid fission and oxidation	$C_2H_2O_2$	
Oxalic acid	Glyoxal oxidation	$C_2H_2O_4$	

Intermediates **1** to **5** were already reported in the literature (Mar Gómez-Ramos *et al.*, 2011). The formation of intermediate **1** indicates that SMX ozonation starts with a hydroxylation of the phenyl ring, while that of the isoxazole ring generates intermediate **2**. An m/z of 160 ($C_4H_4N_2O_3S$) suggests a loss of an aniline group, an m/z of 156 ($C_6H_6NO_2S$) - a loss of isoxazole ring along with two hydroxyl groups, and an m/z of 108 ($C_6H_7N_2$) - a release of SO_2 and isoxazole ring.

Reportedly, photo-Fenton (Beltra *et al.*, 2009) and photocatalytic (Hu *et al.*, 2007) oxidation of sulfamethoxazole also produce this intermediate, which should arise from an oxidation of the double bond in the isoxazole ring. Intermediates **3** and **4** displayed similar m/z values but different retention times. Their oxidation gave rise to m/z 174 derivative (nitric oxide group on the phenyl ring) and a m/z 122 fragments (nitrogen dioxide group on the phenyl ring), respectively, both via amino group oxidation on the phenyl ring. Oxidation of intermediate **5** generated an m/z 72 and m/z 55 derivatives having an isoxazole-like structure (Mar Gómez-Ramos *et al.*, 2011). This accounts for sulfamethoxazole scission at the S–N (sulphonamide) bond.

It is worth mentioning that intermediate **5** exhibited the highest stability due to its lesser complexity, since it decomposes in more than 13-14 min, as compared to its other counterparts, which disappear after only 10 minutes of ozonation (Fig. 4.8). The evolution in time of the intermediate distribution confirms that hydroxylation of the phenyl and isoxazole rings are the first steps in SMX ozonation.

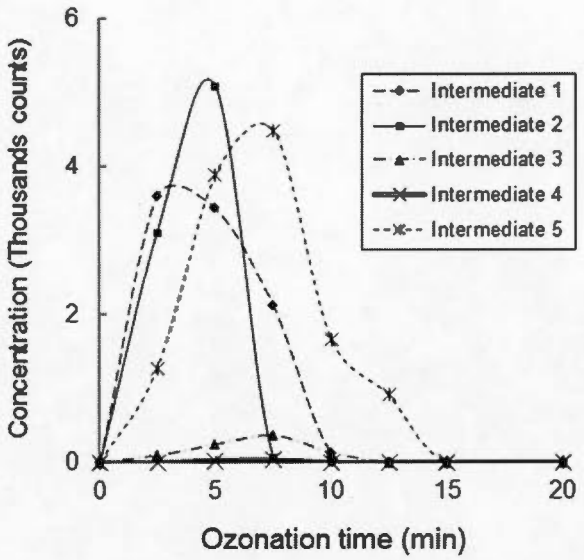


Fig. 4.8. Evolution in time of heavy intermediates in the catalyzed ozonation of sulfamethoxazole. Fe(II)Mt amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88

Identification of smaller intermediates through LC-ToF-MS and comparison of the molecular formula and retention time to reference standards or via the theoretical mass calculator (Table S5) revealed the formation of benzoquinone via the oxidation of the C_1 and C_4 carbon atoms of the phenyl ring. This is supposed to generate ammonium, nitrate and sulphate ions. Further cleavage of benzoquinone ring should give rise to muconic and maleic acids, which, in turn, generate glyoxal and oxalic acid (Fig. 4.9).

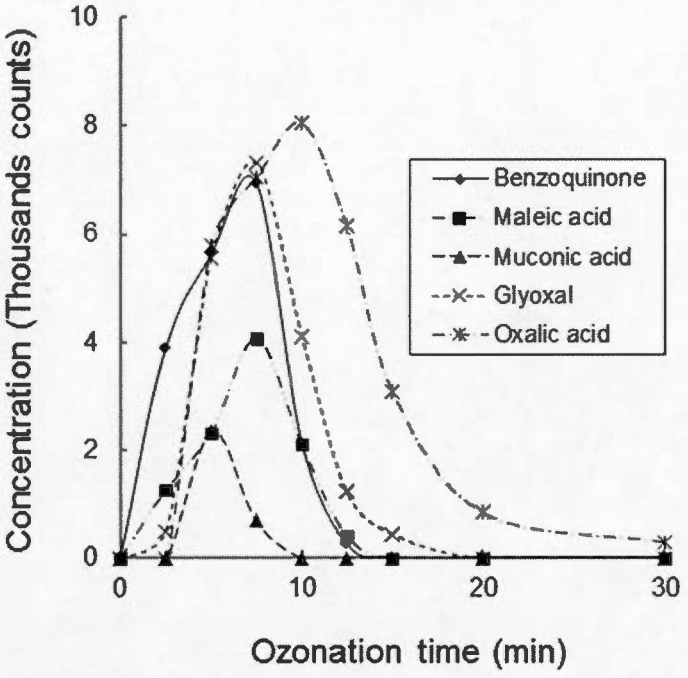
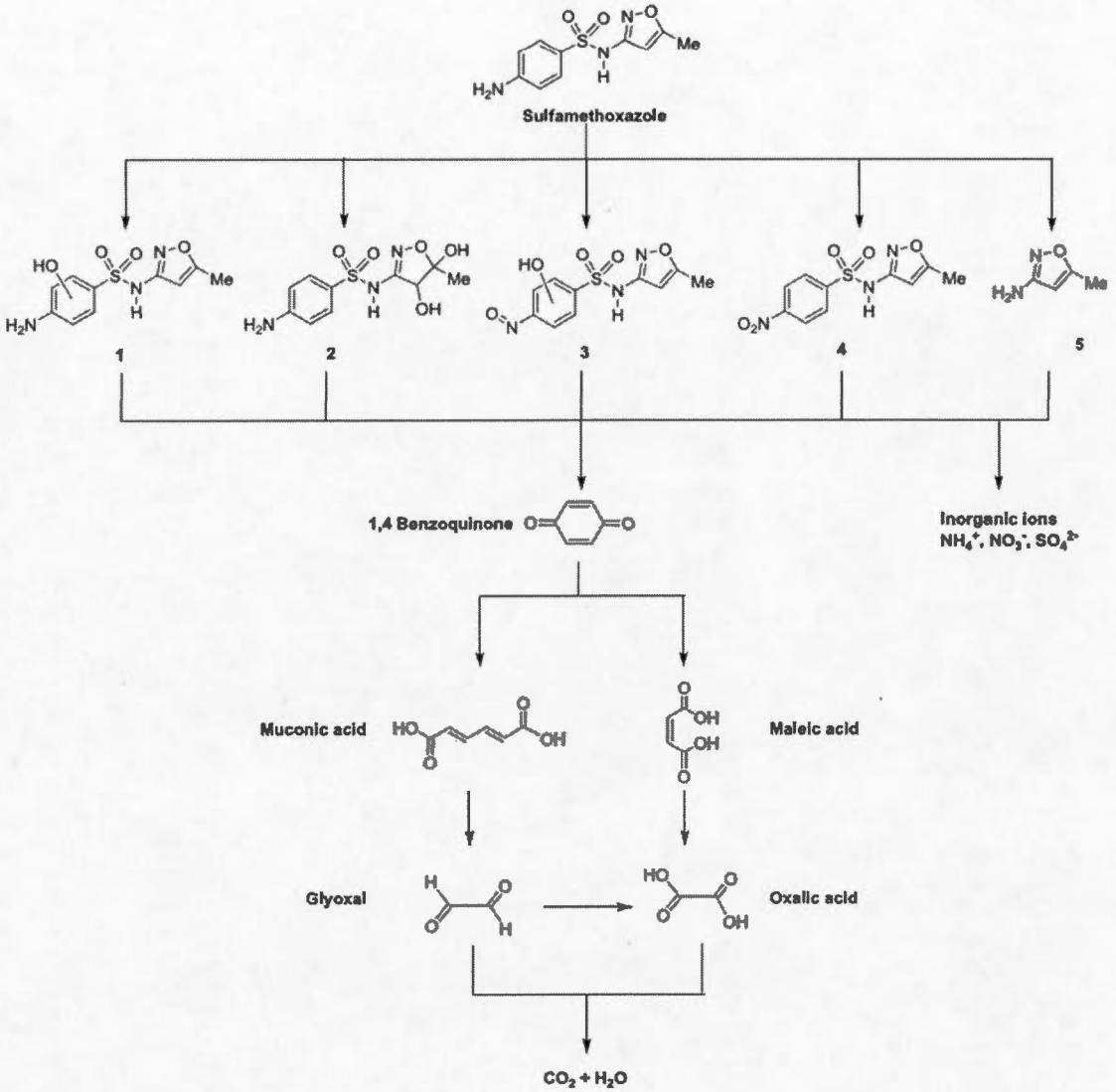


Fig. 4.9. Evolution in time of small size intermediates in the catalyzed ozonation of sulfamethoxazole. Fe(II)Mt amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88.

The latter appear to form even from the first seconds of ozonation. Oxalic acid accumulates at longer ozonation time (10 min) as compared to muconic acid (4-5 min), benzoquinone, maleic acid, and glyoxal (7-8 min). This indicates that most intermediates act as sources of oxalic acid. Small intermediates completely disappeared in less than 12.5 min of ozonation, except glyoxal and oxalic, which still persisted up to 20 and 30 min. This is due to their lower reactivity for oxidation as compared to heavier organic molecules (Fig. S17). The succession in time of the accumulation peaks confirms, once again, that SMX ozonation proceeds first via phenyl ring hydroxylation, isoxazole ring dihydroxylation, phenyl ring hydroxylation combined with amino group oxidation, amino group nitration and isoxazole ring separation (Scheme 4.1).



Scheme 4.1. Suggested decomposition pathway for the catalytic ozonation of sulfamethoxazole.

4.3.3.4 Intermediates in the ozonation of 3-hydroxybenzaldehyde and phenol

The use of the LC-ESI (+) TOF method in the catalytic ozonation of 3-hydroxybenzaldehyde and phenol allowed identifying benzoquinone, glyoxal, muconic, maleic and oxalic acids as common intermediates with sulfamethoxazole (Tables S6-S7). In agreement with previous works on phenol (Azevedo *et al.*, 2006; Liu *et al.*, 2013; Farzadkia *et al.*, 2014; Wang *et al.*, 2012; Santos *et al.*, 2005; Schleinitz *et al.*, 2009; Yang *et al.*, 2010; Poznyak *et al.*, 2006), here also, the succession in time of the accumulation peaks of the identified intermediates (Fig. 4.10 and 4.11) indicates that, except the specific formation of 3-hydroxybenzoic acid and phenol from 3-hydroxybenzaldehyde (Scheme 4.2) and the possible production of catechol, resorcinol and hydroquinone from phenol decomposition (Scheme 4.3), the other steps are similar for both compounds and sulfamethoxazole .

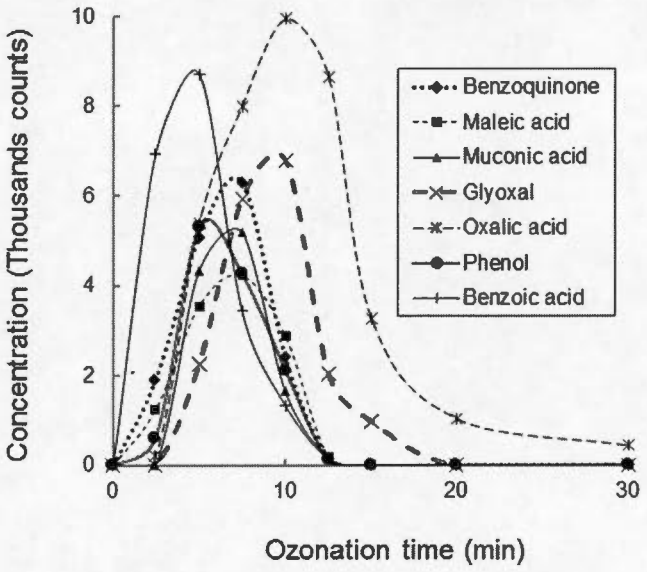


Fig. 4.10. Evolution in time of small size intermediates in the catalyzed ozonation of 3-hydroxybenzaldehyde. Catalyst amount: 1.91 $g.L^{-1}$; C_0=3.10^{-4} M; initial pH=2.88

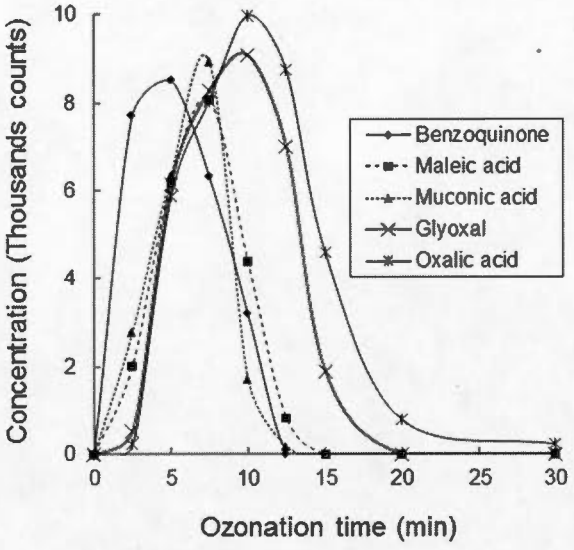
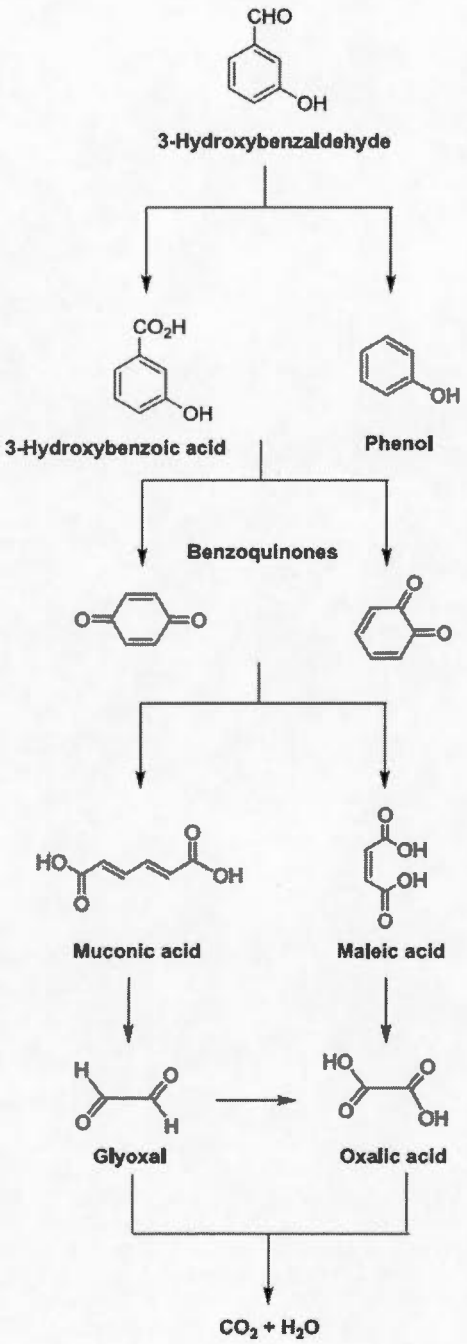
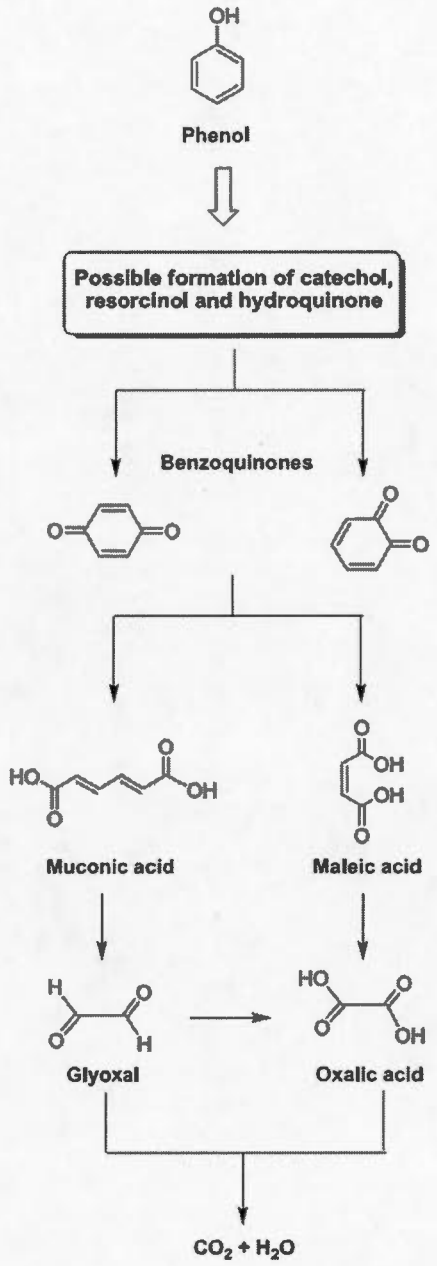


Fig. 4.11. Evolution in time of small size intermediates in the catalyzed ozonation of phenol. Catalyst amount: 1.91 $g.L^{-1}$; C_o=3.10^{-4} M; initial pH=2.88



Scheme 4.2. Suggested decomposition pathway for the catalytic ozonation of 3-hydroxybenzaldehyde



Scheme 4.3. Suggested decomposition pathway for phenol catalytic ozonation

The succession in time of the accumulation peak is explained not only by their consecutive appearance, but also by their decreasing oxidation capacity with decreasing molecular weight and increasing oxidation state. This is well supported by calculations based on a first-order kinetics during the first minutes of ozonation, when the contributions of the side-chain reactions were supposed to be negligible. One also assumed that the ozone concentration was constant, being determined by its solubility in water. Thus, the reaction rate will depend only on the concentration of each organic substrate, which acts as the sole reagent.

4.3.4 Kinetic aspects

In the kinetic study, both the COD and spectrophometric measurements were used for assessing the global rate constant for the global ozonation process and specific rate constant for individual reaction. For all organic substrates, the depletion in time of the main UV-Vis band fit a 1^{st} order kinetics for the first three minutes of ozonation (Fig. S18), as supported by high R^2 values. Linearity loss was noticed for longer ozonation times exceeding 4 min, presumably due to the appearance of side-reactions and (or) consecutive steps. For both kinetical models, the rate constant of ozonation diminished with decreasing molecular weight and oxidation state (Table 4.2). The lowest rate constant was registered for oxalic acid, and the highest for sulfamethoxazole.

Table 4.2. Rate constant and reaction order based on the depletion of the main UV-Vis bands

Organic substrate	First order kinetics				n-order kinetics					
	3 min.		5 min.		3 min.			5 min.		
	k^a	R^2	k^a	R^2	k^a	n	R^2	k^a	n	R^2
Sulfamethoxazole	1.16	0.992	1.03	0.972	0.84	1.9	1.00	1.00	1.7	0.987
3-HO-benzaldehyde	1.02	0.995	0.94	0.984	0.99	1.6	1.00	0.96	1.6	0.988
Phenol	0.98	0.994	0.88	0.979	0.95	1.6	1.00	0.81	1.4	0.982
Chlorobenzene	0.91	0.998	0.84	0.989	0.89	1.6	0.999	0.85	1.6	0,988
Benzoic acid	0.92	0.994	0.82	0.978	0.87	1.6	1.00	0.75	1.4	0.983
4- Nitrobenzoic acid	0.93	0.994	0.81	0.971	0.88	1.6	1.00	0.68	1.3	0.998
4-Nitro phenol	0.91	0.997	0.80	0.981	0.87	1.5	1.00	0.74	1.3	0.987
Oxalic acid	0.40	0.992	0.31	0.949	0.28	1.8	0.998	0.25	1.3	0.960

[a] k is expressed in min^{-1}; n is the reaction order for the n-order kinetics model.

Interestingly, the closest R^2 values to unity were registered for the n-order kinetics model. This indicates that 1st order ozonation reaction, if any, should be accompanied by physical steps, most likely diffusion and adsorption. This is supported by the non-integer values of the reaction order for sulfamethoxazole (1.9), oxalic acid (1.8), 4-nitrophenol (1.5) and the five other organic substrates (1.6). Application of both models to COD resulted in higher linearity for ozonation time below 3 min. (Fig. S19). However, the closest R^2 values to unity suggest a 1st order kinetics for only 4-nitrobenzoic, benzoic and oxalic acids, but a n-order for the other organic substrates. The fact that both models gave close values of the rate constant, and that the reaction order differs from unity (Table 4.3) indicates a predominance of a 1st order chemical step, presumably in the bulk solution, and a weak contribution of diffusion and(or) adsorption during the first 3 min.

Table 4.3. Rate constant and reaction order based on COD depletion.

Organic substrate	First order kinetics				n-order kinetics					
	3 min.		5 min.		3 min.			5 min.		
	k^a	R^2	k^a	R^2	k^a	n	R^2	k^a	n	R^2
Sulfamethoxazole	0.24	0.965	0.20	0.938	0.18	1.4	0.993	0.17	1.1	0.971
Chlorobenzene	0.14	0.858	0.11	0.750	0.17	1.1	0.937	0.17	1.1	0.922
3-HO-benzaldehyde	0.28	0.992	0.26	0.985	0.22	1.3	1.000	0.23	1.4	0.979
4- Nitrobenzoic acid	0.22	0.996	0.18	0.948	0.15	1.1	0.986	0.15	1.1	0.932
4-Nitro phenol	0.13	0.908	0.09	0.769	0.13	0.7	1.000	0.13	0.8	0.936
Benzoic acid	0.20	0.997	0.20	0.973	0.20	1.4	0.895	0.18	1.1	0.828
Phenol	0.19	0.941	0.14	0.800	0.15	1.3	0.943	0.14	1.1	0.937
Oxalic acid	0.07	0.977	0.05	0.922	0.15	1.7	0.933	0.15	1.5	0.928

[a] k is expressed in min^{-1}; n is the reaction order for the n-order kinetics model. The rate constants (k, min^{-1}) have been calculated based on first-order kinetic model for relative COD (See supporting information).

As expected, COD depletion kinetics showed lower rate constants, the lowest value being obtained for oxalic acid (0.07 min^{-1}), in agreement with its low reactivity towards oxidation. Calculations based on HPLC-MS measurements allowed plotting the reaction rate expressed in terms of ($\Delta X/\Delta t$) as a function of X, where X is the conversion of each organic substrate taken as probe molecule. High linearity (Fig. S20-S22) and R^2 values close to unity (Table 4.4) clearly demonstrate that the formation of all intermediates from sulfamethoxazole, 3-hydroxy-benzaldehyde and phenol obeys a 1^{st} order kinetics for the first 3 min. The high rate constants of 2.33-3.41 min^{-1} confirm that ozonation is initially quite fast, and adsorption, if any, plays a minor role. The equations used for calculation of kinetic data were described in Appendix K.

Table 4.4. Rate constant and reaction order based on concentration evolution determined by HPLC-MS.

Organic substrate	Compound	3 min.		5 min.		3 min.			5 min.		
		k^a	R^2	k^a	R^2	k^a	n	R^2	k^a	n	R^2
Sulfamethoxazole	Intermediate 1	2.72	0.999	2.60	0.998	0.02	4.2	0.950	0.006	5.4	0.899
	Intermediate 2	2.87	1.000	2.65	0.990	0.02	3.5	0.962	0.009	4.8	0.878
	Intermediate 3	2.42	0.968	1.79	0.910	0.04	2.4	0.997	0.057	1.7	0.954
	Intermediate 4	2.59	0.997	2.47	0.996	0.03	2.7	0.917	0.006	4.6	0.711
	Intermediate 5	3.09	0.995	2.53	0.934	0.05	2.2	1.000	0.026	3.1	0.972
	Benzoquinone	2.67	0.994	2.43	0.984	0.03	3.1	0.985	0.017	3.7	0.958
	Maleic acid	2.80	0.993	2.49	0.973	0.05	2.1	0.996	0.038	2.3	0.980
	Muconic acid	2.33	0.991	2.40	0.990	0.02	2.4	0.869	0.030	2.2	0.855
	Glyoxal	2.86	0.995	2.88	0.994	0.07	1.6	0.929	0.052	1.3	0.724
	Oxalic acid	2.95	0.999	2.78	0.993	0.03	2.5	0.930	0.021	2.6	0.916
3-HO-benzaldehyde	Benzoquinone	3.16	0.969	2.37	0.847	0.03	3.4	0.986	0.083	1.1	0.862
	Benzoic acid	3.09	0.999	2.86	0.988	0.02	3.8	0.967	0.022	3.3	0.958
	Muconic acid	3.05	0.996	2.87	0.990	0.03	2.9	0.931	0.022	2.9	0.926
	Maleic acid	3.23	0.981	2.71	0.919	0.04	2.7	0.977	0.050	1.9	0.956
	Phenol	2.41	0.994	2.33	0.993	0.06	1.8	0.943	0.048	1.8	0.937

	Glyoxal	3.33	0.968	2.57	0.912	0.04	2.4	0.998	0.058	1.7	0.912
	Oxalic acid	3.06	0.999	2.98	0.996	0.03	2.8	0.952	0.027	2.4	0.882
	Benzoquinone	2.88	0.998	2.69	0.991	0.02	4.1	0.953	0.015	3.8	0.944
	Muconic acid	3.24	0.990	2.87	0.959	0.02	4.1	0.979	0.030	2.9	0.931
Phenol	Maleic acid	2.42	0.968	2.58	0.953	0.08	1.0	0.997	0.096	1.0	0.872
	Glyoxal	2.77	0.999	2.74	0.999	0.04	1.6	0.832	0.099	0.8	0.804
	Oxalic acid	3.41	0.996	3.33	0.993	0.03	2.7	0.952	0.018	3.4	0.946

[a] k is expressed in min^{-1}; n is the reaction order for the n-order kinetics model. The rate constants (k) have been calculated based on first-order kinetic model for the production yield of intermediates (See supporting information).

The linearity loss and rate constant decrease after 5 min of ozonation indicate a process attenuation, presumably due to the appearance of kinetic-controlling steps such as adsorption and diffusion. Such an attenuation was more pronounced for the formation of some acidic intermediates, most likely due to weak interactions with the catalyst surface. This remains to be elucidated.

The rate constant for the formation of oxalic acid increased from 2.95 (from sulfamethoxazole) to 3.06 (from 3-hydroxy-benzaldehyde) and 3.41 (from phenol). This indicates a faster formation of oxalic acid from phenol than from 3-hydroxy-benzaldehyde and sulfamethoxazole, due to increasing step number in the degradation process.

4.4 Conclusion

Fe^{2+}-Montmorillonite acted as effective catalyst for total mineralization of sulfamethoxazole and other aromatic substrates by quick ozonation under optimum conditions and optimum iron content. Ozonation generates a wide variety of intermediates, some of them being common to different organic substrates. Elucidation of the decomposition pathways of the different aromatic compound investigated allowed understanding the different steps involved in the overall decomposition pathway of SMX. The succession in time of the accumulation peaks of the identified intermediates suggests that ozonation of sulfamethoxazole starts mainly via phenyl ring hydroxylation, isoxazole ring dihydroxylation, phenyl ring hydroxylation and amino group oxidation and amino group nitration. The accumulation of small size intermediates reflects their lower reactivity for oxidation as compared to bulkier and (or) less oxidized counterparts. Kinetic calculations revealed that ozonation starts in the bulk solution, while adsorption is progressively

enhanced in time by the progressive appearance of intermediates. These findings allow envisaging convenient and total mineralization of any organic pollutant by low cost clay-based catalysts.

REFERENCES

American Society for Testing and Materials. (1976). Annual Book of ASTM Standards. 31-Water, Standard D 1252-67 (p. 473) West Conshohocken: ASTM International.

Azevedo, E. B., Radler de Aquino Neto, F. and Dezotti, M. (2006). Lumped kinetics and acute toxicity of intermediates in the ozonation of phenol in saline media. *Journal of Hazardous Materials*, B128, 182–191.

Azzouz , A. (2012). Advances in Oxidative Decomposition of Oxalic Acid in Aqueous Media, in: J. C. Taylor (Eds.), Advances in Chemistry Research (p. 1 – 31). New York :Nova-Publishers.

Azzouz, A., Kotbi, A., Niquette, P., Sajin, T., Ursu, A.-V., Rami, A., Monette, F. and Hausler, R. (2010). Ozonation of oxalic acid catalyzed by ion-exchanged montmorillonite in moderately acidic media. *Reaction Kinetics mechanisms and catalysis*, 99, 289 – 302.

Baquero, F., Luis Martinez, J. and Canton, R. (2008). Antibiotics and antibiotic resistance in water environments. *Current Opinion in Biotechnology,* 19, 260–265.

Beltra, F. J., Aguinaco, A. and Garcia-Araya, J.-F. (2009). Mechanism and kinetics of sulfamethoxazole photocatalytic ozonation in water. *Water Research*, 43, 1359–1369.

Beltran, F.J., Rivas, F.J. and Gimeno, O. (2005). Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water. *Journal of Chemical Technology and biotechnology*, 80, 973–984.

Booth, G. (2005). *Aromatic nitro compounds, Ullmann's Encyclopedia of Industrial Chemistry*, (p. 9-11). Electronic Release, Weinheim: Wiley-VCH.

Boudreau, J., Bejan, D., Li, S. and Bunce, N.-J. (2010). Competition between Electrochemical Advanced Oxidation and Electrochemical Hypochlorination of Sulfamethoxazole at a Boron-Doped Diamond Anode. *Industrial and Engineering Chemistry Research*, 49, 2537–2542.

Brecken-Folse, J.-A., Mayer, F.-L., Pedigo, L.-E. and Markin, L.-L. (1994). Acute Toxicity of 4-Nitrophenol and 2,4-Dinitrophenol, Terbufos and Tricholorfon to Grass Shrimp and Sheepshead Minnows as Affected by Salinity and Temperature. *Environmental Toxicology and Chemistry,* 13, 67-77.

Bruhne, F. and Wright, E. (2005). *Benzaldehyde, Ullmann's Encyclopedia of Industrial Chemistry*, (p. 9-10). Electronic Release, Weinheim: Wiley-VCH.

Chatterjee, D., Dasgupta, S., Dhodapkar, R.-S. and Raob, N.-N. (2006). Simultaneous degradation of non-emissive and emissive dyes on visible light illuminated TiO2 surface. *Journal of Molecular Catalysis A: Chemical*, 260, 264-268.

Chiwosha, S.-D., Abrams, S.-R., Ambrose, S.-J., Cutler, A.-J., Loewen, M., Ross, A.-R. and Kermode, A.-R. (2033). A method for profiling classes of plant hormones and their metabolites using liquid chromatography –electrospray ionization tandem mass spectrometry. *The plant journal*, 35, 405-417.

Dantas, R.-F., Contreras, S., Sans, C. and Esplugas, S. (2008). Sulfamethoxazole abatement by means of ozonation. *Journal of Hazardous Materials,* 150, 790–794.

Daud , N.K., Ahmad , M.A. and Hameed , B.H. (2010). Decolorization of Acid Red 1 dye solution by Fenton-like process using Fe–Montmorillonite K10 catalyst. *Chemical Engineering Journal,* 165, 111–116.

Diez, M.C. (2010). Biological aspects involved in the degradation of organic pollutants. *Journal of plant Nutrition and Soil Science,* 10, 244 – 267.

Dirany, A., Aaron, S.-E., Oturan, N., Sirés, I., Oturan, M.-A. and Aaron, J.-J. (2011). Study of the toxicity of sulfametho xazole and its degradation products in water by a bioluminescence method during application of the electro-Fenton treatment. *Analytical and Bioanalytical Chemistry,* 400, 353–360.

Dirany, A., Sirés, I., Oturan, N. and Oturan, M.-A. (2010). Electrochemical abatement of the antibiotic sulfamethoxazole from water. *Chemosphere,* 81, 594 – 602.

Eaton, A.-D. and Franson, M.-A.-H. (1975). Standard Methods for the Examination of Water and Wastewater. 14th Ed. Method 508, (p. 550), APHA-AWWA publication.

Elsousy, K., Hussen, A., Hartani, K. and Elaila, H. (2007). Elimination of Organic Pollutants using Supported Catalysts with Hydrogen Peroxide. *Jordan Journal of Chemistry*, 2, 97 – 103.

F.-J., Beltran, Rivas, F.-J. and Montero de Espinosa, R. (2002). Catalytic ozonation of oxalic acid in an aqueous TiO_2 slurry reactor. *Applied Catalysis B: Environmental,* 39, 221-231.

Farzadkia, M., Dadban Shahamat, Y., Nasseri, S., Mahvi, A. H., Gholami, M. and Shahryari, A. (2014). Catalytic ozonation of phenolic wastewater: Identification and toxicity of intermediates. *Journal of Engineering*, http://dx.doi.org/10.1155/2014/520929.

Giordano, G., Perathoner, S., Centi, G., De Rosa, S., Granato, T., Katovic, A., Siciliano, A., Tagarelli, A. and Tripicchio, F. (2007). Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts. *Catalysis Today* 124, 240–246.

Gonzalez, O., Sans, C. and Esplugas, S. (2007). Sulfamethoxazole abatement by photo-Fenton Toxicity, inhibition and biodegradability assessment of intermediates. *Journal of Hazardous Materials*, 146, 459–464.

Guo, Y., Yang, L., Cheng, X. and Wang X. (2012). The Application and Reaction Mechanism of Catalytic Ozonation in Water Treatment. *Journal of Environmental and Analytical Toxicology*, 2, 1–6.

Hu, L., Flanders, P.-M., Miller, P.-L. and Strathmann, T.-J. (2007). Oxidation of sulfamethoxazole and related antimicrobial agents by TiO_2 photocatalysis. *Water Research*, 41, 2612–2626.

Ito, H., Kotake, T. and Masai, M. (1996). In vitro Degradation of oxalic acid by human feces. *International Journal of Urology*, 3, 207–211.

Kasper, D.-L., Braunwald, E., Hauser, S., Longo, D., Jameson, J.-L. and Fauci, A.-S. (2004). *Harrison's Principles of Internal Medicine*, 16th Edition, (p. 618). New York: McGraw-Hill Companies,Inc.

Kitsopoulos, K.-P. (1999). Cation exchanged capacity (CEC) of zeolitic volcaniclastic materials: Applicability of the ammonium acetate saturation (AMAS) method, *Clays and Clay Minerals*, 47, 688-696.

Kjellström, T., Lodh, M., McMichael, T., Ranmuthugala, G., Shrestha, R. and Kingsland, S. (2006). Disease Control Priorities in Developping Countries, (p. 817 – 833). Washington DC: oxford university press.

Li, S., Bejan, D. and Bunce, N.-J. (2008). Mixed first and zero order kinetics in the electrooxidation of sulfamethoxazole at a boron-doped diamond (BDD) anode. *Journal of Applied Electrochemistry*, 38, 151–159.

Liu, Y., Zhu, Y., Xu, J., Bai, X., Zong, R. and Zhu, Y. (2013). Degradation and mineralization mechanism of phenol by $BiPO_4$ photocatalysis assisted with H_2O_2. *Applied Catalysis B: Environmental,* 142– 143, 561– 567.

Maki, T. and Takeda, K. (2005). *Benzoic Acid and Derivatives, Ullmann's Encyclopedia of Industrial Chemistry*, (p. 4-7). Electronic Release, Weinheim: Wiley-VCH.

Mar Gómez-Ramos, M., Mezcua, M., Agüera, A., Fernández-Alba, A. R., Gonzalo, S., Rodríguez, A. and Rosal, R. (2011). Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution. *Journal of Hazardous Materials,* 192, 18–25.

Martin de Vidales, M., Robles-Molina, J., Dominguez-Romero, J.-C., Canizares, P., Saez, C., Molina-Diaz, A. and Rodrigo, M.-A. (2012). Removal of sulfamethoxazole from waters and wastewaters by conductive-diamond electrochemical oxidation. *Journal of Chemical Technology and Biotechnology,* 87, 1441–1449.

Moheb, A., Ibrahim, R.-K., Roy, R., Sarhan, F. (2011). Changes in wheat leaf phenolome in response to cold acclimation. *Phytochemistry*, 72, 2294–2307.

Munter, R., Trapido, M., Veressinina, Y. and Goi, A. (2006). Cost Effectiveness of Ozonation and AOPs for Aromatic Compound Removal from Water: A Preliminary Study. *Ozone: Science and Engineering* , 28, 287–293.

Negrel, P., Blessing, M., Millot, R., Giraud, E.P. and Innocent, C. (2012). Isotopic methods give clues about the origins of trace metals and organic pollutants in the environment. *Trends in Analitical Chemistry*, 38, 143 – 153.

Nidheesh , P.V. and Gandhimathi, R. (2012). Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination* , 299, 1 – 15.

Pang, W., Yang, H., Wu, Z., Huang, M. and Hu, J. (2009). LC-MS–MS in MRM Mode for Detection and Structural Identification of Synthetic Hypoglycemic Drugs Added Illegally to Natural Anti-Diabetic Herbal Products. *Chromatographia*, 70, 1353–1359.

Park, J.-N., Wang, J., Choi, K.-Y, Dong, D.-Y., Hong, S.-I. and Lee, C.-W. (2006). Hydroxylation of phenol with H_2O_2 over Fe^{2+} and/or Co^{2+} ion-exchanged NaY catalyst in the fixed-bed flow reactor. *Journal of Molecular Catalysis A: Chemical,* 247, 73–79.

Park, J. S., Brown, M. T. and Han, T. (2010). Phenol toxicity to the aquatic macrophyte Lemna paucicostata, *Aquatic Toxicology,* 106– 107, 182– 188.

Poznyak, T., Tapia, R., Vivero, J. and Chairez, I. (2006). Effect of pH to the decomposition of aqueous phenols mixture by ozone. *Journal of the Mexican Chemical Society,* 50, 28–35.

Ren, L., Li, G., Han, Y.-C., Jiang, D.-H. and Huang, H.-C. (2007). Degradation of oxalic acid by Coniothyrium minitansand its effects on production and activity of β-1,3-glucanase of this mycoparasite. *Biological Control,* 43, 1–11.

Rodayan, A., Roy, R. and Yargeau, V. (2010). Oxidation products of sulfamethoxazole in ozonated secondary effluent. *Journal of Hazardous Materials,* 177, 237–243.

Rossberg, M., Lendle, W., Pfleiderer, G., Togel, A., Dreher, E.-L., Langer, E., Rassaerts, H., Kleinschmidt, P., Cook, R., Beck, U., Lipper, K.-A., Torkelson, T., Loser, E., Beutel, K. and Mann, T. (2005). *Chlorinated Hydrocarbons, Ullmann's Encyclopedia of Industrial Chemistry*, (p. 112-114). Electronic Release, Weinheim: Wiley-VCH.

Roy, S., Vashishtha, M., Saroha, A.-K. (2010). Catalytic Wet Air Oxidation of Oxalic Acid using Platinum Catalysts in Bubble Column Reactor: A Review. *Journal of Engineering Science and Technology Review,* 3, 95-107.

Santos, A., Yustos, P., Cordero, T., Gomis, S., Rodriguez, S. and Garcia-Ochoa, F. (2005). Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization. *Catalysis Today*, 102–103, 213–218.

Schleinitz, K. M., Schmeling, S., Jehmlich, N., Bergen, M., Harms, H., Kleinsteuber, S., Vogt, C. and Fuchs, G. (2009). Phenol degradation in the strictly anaerobic iron-reducing bacterium geobacter metallireducens. *Applied and Environmental Microbiology,* 75, 3912–3919.

Segarra, G., Jauregui, O., Casanova, E. and Trillas, I. (2006). Simultaneous quantitative LC–ESI-MS/MS analyses of salicylic acid and jasmonic acid in crude extracts of Cucumis sativus under biotic stress. *Phytochemistry*, 67, 395–401.

Shahidi, D., Roy, R., Azzouz, A. (2014). Total removal of oxalic acid via synergistic parameter interaction in montmorillonite catalyzed ozonation. Journal of Environmental Chemical Engineering, 2, 20-30.

Sharma, V. K., Mishra, S. K. and Ray, A. K. (2006). Kinetic assessment of the potassium ferrate(VI) oxidation of antibacterial drug sulfamethoxazole. *Chemosphere* 62, 128–134.

Smith, M. T. (2010). Advances in understanding benzene health effects and susceptibility. *Annual Review of Public Health*, 31, 133–48.

Trovo, A. G., Nogueira, R. F., Aguera, A., Fernandez-Alba, A. R., Sirtori, C. and Malato, S. (2009). Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation. *Water Research,* 43, 3922–3931.

Wang, C. M., Lai, T. L., Chiou, J. Y. Z., Ho, K. F., Shu, Y. and Wang, C. B. (2012). Degradation of phenol over nickel oxides: Influence of the preparation routes, Asia Pacific Conference on Environmental Science and Technology. *Advances in Biomedical Engineering*, 6, 515 – 521.

Wang, D. and Fiessel, W. (2008). Evaluation of media for simultaneous enumeration of total coliform and Escherichia coli in drinking water supplies by membrane filtration techniques. *Journal of Environmental Science*, 20, 273–277.

Yang, L. P., Hu, W.-Y., Huang, H. M. and Yan, B. (2010). Degradation of high concentration phenol by ozonation with ultrasonic irradiation. *Desalination and Water Treatment*, 21, 87–95.

Zhao, L., Sun, Z., Ma, J. and Liu, H. (2009). Enhancement Mechanism of Heterogeneous Catalytic Ozonation by Cordierite-Supported Copper for the Degradation of Nitrobenzene in Aqueous Solution. *Environmental Science and Technology,* 43, 2047–2053.

Zhu, K.-Z., Liu, C.-B., Ye, X.-K. and Wu, Y. (1998). Catalysis of hydrotalcite-like compounds in liquid phase oxidation: (I) phenol hydroxylation. *Applied Catalysis A: General,* 168, 365–372.

CHAPTER V

GLOBAL CONCLUSION

Effective water treatments without traces of persistent hazardous by-products or toxins can be achieved through catalytic ozonation. The use of montmorillonite is an essential requirement for achieving total mineralization of oxalic acid via ozonation in water at ambient temperature within reasonable reaction times. The crude and Na-exchanged clay samples displayed relatively smaller but still appreciable catalytic activity towards oxalic acid ozonation. Such a result is of great interest, since the clay purification can be avoided. A key-step in achieving the total mineralization resides in the rigorous choices of adequate solid catalysts to be used in optimum operating conditions. The present study allows drawing a series of conclusions, which will be deeply analyzed further:

- Effective water treatments without traces of persistent hazardous by-products or toxins can be achieved through suitable oxidative processes.
- A key-step in achieving the total mineralization resides in the rigorous choices of adequate solid catalysts to be used in optimum operating conditions.
- The application of montmorillonite is an essential requirement to achieved high decomposition yields of oxalic acid via ozonation in water at ambient temperature.
- The role of montmorillonite must involve not only the catalytic effect of the exchangeable cation but also the contribution of adsorption on the clay mineral surface.

- Co(II) and Fe(II) exchanged montmorillonites turned out to be effective catalyst in the ozonation of oxalic acid. Fe(II)Mt gives higher decomposition yields than Co(II)Mt.
- The initial pH and catalyst amount showed significant individual effects and interaction.
- The detrimental effect of increasing pH and catalyst amounts must be due to clay compaction, which is assumed to hinder the cation mobility and adsorption contribution.
- Total removal of oxalic acid was achieved at pH 2.87 with 1.88 $g.L^{-1}$ of Co(II)Mt, or at pH 2.88 with 1.91 $g.L^{-1}$ of Fe(II)Mt.
- LC-MS analyses revealed that ozonation generates a wide variety of intermediates, which are common at the last steps in ozonation of 3-hydroxybenzaldehyde, phenol and sulfamethoxazole .
- The increase of the iron content turned out to enhance the decomposition yield but only up to an optimum ion exchange level.
- The first steps in the ozonation of sulfamethoxazole involve mainly phenyl ring hydroxylation, isoxazole ring di-hydroxylation, phenyl ring hydroxylation and amino group oxidation and nitrilation.
- Benzoquinone, muconic acid, maleic acid, glyoxal and oxalic acid are common intermediates of sulfamethoxazole , 3-hydroxybenzaldehyde, and phenol catalytic ozonation.
- The accumulation of small size intermediates was attributed to their higher chemical resistance against oxidation.
- The final products of mineralization (CO_2, SO_x, and NO_x) may be retreated into added-value derivatives.

A deep analysis of the main observations made in the different steps of this research allows explaining the beneficial effect of optimum pH and catalyst concentration in

terms of specific behavior of clay mineral in water. The detrimental effect of increasing pH and catalyst amounts is due to clay compaction and decrease in cation mobility. In other words, even though ozonation in the presence of clay minerals under acid conditions does not particularly favor hydroxyl radical pathway, slight ion-exchange on the catalyst surface, and surface interaction between Fe^{2+} or Co^{2+} with traces of oxalic acid is supposed to generate very reactive cation-oxalate species towards ozone in both its adsorbed or dispersed forms (insoluble bubbles and dissolved). In our ozonation attempts, Fe(II)Mt acted as effective catalyst for total mineralization of bulkier molecules such as sulfamethoxazole and aromatic molecules. Elucidation of the decomposition pathways of the different aromatic compound investigated in this thesis allowed understanding the different steps involved in the overall decomposition pathway of sulfamethoxazole. The accumulation of small size oxygenated intermediates reflects their higher chemical resistance, refractory character and reluctance for oxidation as compared to their less oxidized parent molecules. Kinetic calculations revealed that ozonation starts in the bulk solution, while adsorption is progressively enhanced in time by the progressive appearance of intermediates. The appearance of carboxylic acids may be regarded as being an essential requirement for the formation of Metal (II)-carboxylate in the vicinity of the solid surface. Such species are known to be very reactive towards ozone. As expected, the required ozone dose for oxalic acid mineralization is higher than that for bulky molecules and this proves the primary hypothesis of ozonation for refractory short-chain molecules versus bulky organic matter. These findings open promising prospects for low cost and convenient water treatment through fast ozonation at ambient temperature for total mineralization of organic pollutants without residual traces of persistent hazardous derivatives.

The main findings of this research show that ozonation first triggers with molecular ozone (1^{st} order kinetics) until adsorption imposes changes in the ozonation pathway

(n-order kinetics). Thus, the involvement of the n-order kinetics is a clear evidence of the additional contribution of other reactive species beside that of molecular ozone. Such an oxidative water treatment may be a promising route notwithstanding the high energy consumption. The latter can be significantly reduced through synergistic parameter interaction. Such an approach has never been tackled so far. This helps understand why nature can self-regenerate, inasmuch as small concentrations of organic pollutants can been photo-degraded by sedimentary sludges in oxygenated shallow waters and more particularly in tiny water streams.

It is worth reminding that the total mineralization of organic pollutants was the main target of the present work, without taking into account the further application (drinking water or wastewater treatment). This involves another objective narrowly connected to the first one, and which resides in the assessment of the optimum conditions for such a purpose.

Once known, it is up to technicians, engineers and (or) politicians to decide whether catalytic ozonation is strongly recommended for drinking water (and it is) or too expensive for treating wastewaters before their release in nature. If both human health and biodiversity are put at the same priority level, ozonation appears as being unavoidable, regardless to the operating costs. Many politics did not proceed so. This is a politic vision that can differ from people to others and from a country to another. Non ozonated wastewaters produce unavoidably indirect effects of environment contamination on human health, as long as humanity still remains at the top of the food chain. Is ozonation still expensive or not expensive for wastewater treatment? The answer to this question depends on the economic and technological context, which evolves in time.

SUGGESTIONS FOR FUTURE WORK

The promising results regarding organic pollutants degradation by means of catalytic ozonation obtained in this thesis encourages us to propose some ultimate experiments. This will allow economizing the production and application of ozone in waste-water treatment facilities. In this regard, the following recommendations may be suggested as the fuel for further research in this field.

1. Application of gas sensors: It is recommended to apply a CO_2 gas sensor for determination of mineralization yield instead of time consuming COD tests, since VOC may enter to gas phase without being mineralized. Application of an ozone gas sensor can also be useful to determine and to optimize the required ozone dose for mineralization of a special type of pollutant solution. This can economize the expenses of costly ozone production.

2. Toxicity Testing: To obtain minimum ozone dose, required for a determined decrease in waste-water toxicity is another way to economize the decontamination processes. For this purpose, application of Microtox Acute Toxicity test to study the toxicity of the waste-water as a function of ozonation time may be useful.

3. Application of a continuous ozonation set up: One can propose to design a continuous catalytic ozonation set up by applying packed columns using special packing materials. This will permit to investigate possible mass transfer limitations. A cost analysis will then be fulfilled to study the feasibility of the proposed method in industrial scale processes.

4. Kinetics study and the role of adsorption: The low ozone solubility and the applicability of the 1^{st} order model for short ozonation times, and accurate assessment of the contribution of reagents adsorption in the global ozonation process need to be deeply investigated. Also it should be clarified that if a quaternary ozone-cation-clay-organic substrate contact is strongly required for effective ozonation processes. The synergy between the solid surface and Fe^{2+} cation was assessed herein in terms of "pH-clay amount" interaction, but still remains to be elucidated.

5. Understanding the role of pH on reaction mechanism: It is almost clear that ozonation in moderately acidic media takes place in both the bulk solution, on ozone bubble interface and clay surface A possible future direction in this regard should involve investigations of isolated ozone–clay, ozone-Fe^{2+} , substrate-clay and substrate-Fe^{2+} interactions. The use of different radical quenchers and electron paramagnetic resonance may also contributes in identifying the main reactive species arising from these interactions. This is real challenge, whose solutions may help understanding the role of pH levels in the mobility and retention of all the involved species.

APPENDIX A

OA OZONATION PROCEDURE AND PRODUCT ANALYSIS

Ozone was bubbled in an aqueous oxalic acid solution using two different procedures: 1. within a batch reactor, i.e. a flask coupled to a reflux cooling device to avoid liquid loss by evaporation (Fig. S1.).

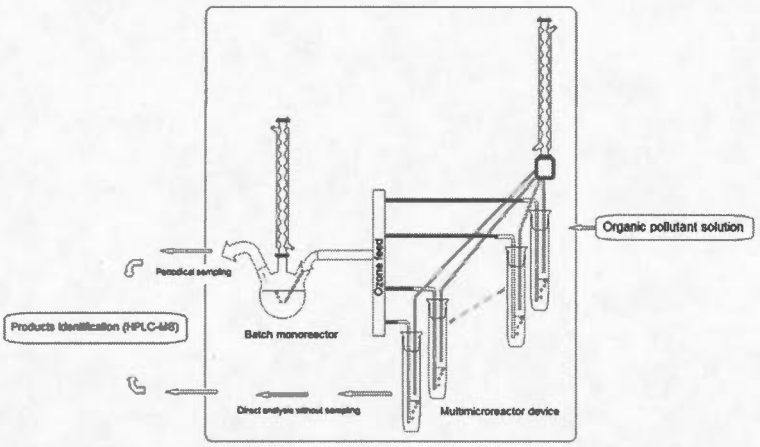


Fig. S1. Setup for the ozonation experiments. Small number of micro-samples were taken from the reaction mixture, so that the total amount removed (less than 10%) does not influence greatly the evolution in time of the ozonation process; 2. When higher number of samples is needed so as the total sample amount exceeds 10%, no sampling was made, and a series of small and similar reaction mixtures were simultaneous ozonated at the same ozone throughput for different bubbling times. The samples were further analyzed through quantitative COD measurements and qualitative HPLC-MS identification of the reaction products and intermediates.

APPENDIX B

SUPPLEMENTARY DETAILS ON CATALYST PREPARATION AND CHARACTERIZATION

Montmorillonite-rich material (NaMt) with 95 wt. % purity and 2.46 Si/Al weight ratio was obtained through purification of commercial crude bentonite supplied by Aldrich with a 2.58 Si/Al weight ratio. The purification procedures includes ultrasound treatment for improving clay dispersion in water, ozone treatment for removing organic impurities, short acid treatment with 0.01 M HCl for decomposing carbonates if any, repeated settling in distilled water, calcination at 400°C, full ion-exchange through repeated impregnations in 4 M NaCl aqueous solution at 70-80°C. NaMt was repeatedly dialyzed overnight in deionized water (40–50°C) though a cellophane film in order the remove the physically sorbed salt excess, then filtered, and air-dried overnight at 25°C. The supernatant was analyzed by the conventional $AgNO_3$ test till the total disappearance of the AgCl precipitate.Except loss on calcination not exceeding 6-7 wt%, no structural change in the montmorillonite framework. NaMt displayed a cation exchange capacity of 100-105 meq/100 g. Other ion-exchanged samples were obtained by impregnating 40 g of dry NaMt in 1 L of various fresh aqueous 1 M solution of nitrate metal salt (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}). Energy dispersion X-rays analysis was achieved by means of an EDAX-Sapphire instrument coupled to a Hitachi S-4300SE/N-VP SEM equipment, using a Si(Li) crystal and an active surface of 10 mm^2). X-ray fluorescence analysis showed changes in the chemical composition of the starting material after purification (Table S1). Fe(II)Mt samples with different iron contents were obtained by impregnating NaMt with aqueous $FeCl_2$ solutions for different contact times of 1-7 hours. The iron content of the Fe(II)-Mt catalysts increased from 0% (pure NaMt) to 27.3%, 52.5%,

79.5%, and 100% of the cation exchange capacity (CEC). XR-fluorescence gave similar Fe(II) content in fully ion-exchanged montmorillonite as the value of the CEC provided by ion-exchange isotherm measurements. The latter was also used for accurate assessment of the M(II) cation contents with a relative error not exceeding 2%.

Table S1. Chemical composition and some features of the crude bentonite used as starting material and purified montmorillonite

Sample	Bentonite	NaMt
Chemical composition*	wt %	wt %
O	48.59%	48.94%
Na	2.01%	1.77%
Mg	1.54%	1.43%
Al	11.93%	12.37%
Si	30.73%	31.17%
S	0.24%	287 ppm
K	0.36%	0.12%
Ca	1.12%	0.64%
Ti	949 ppm	965 ppm
Fe	2.58%	2.75%
Mn	95 ppm	-
Zn	53 ppm	-
Sr	112 ppm	-
Si/Al (wt)*	2.575	2.519
d_{001} basal spacing (Å)**	13.1	10.3
Montmorillonite content (wt %)**	79	93
CEC ($meq.g^{-1}$) at neutral pH	0.64	1.00
BET surface area ($m^2.g^{-1}$)	50	59

* The chemical composition and Si/Al ratio were determined through XRF analysis.
** The d_{001} basal spacing and montmorillonite content were assessed by XRD and mineralogical calculations.

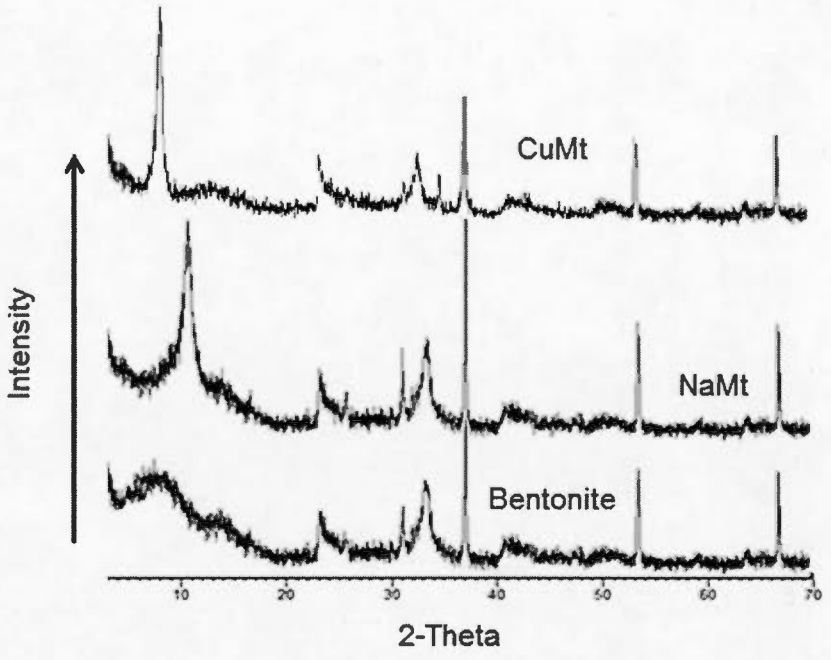


Fig. S2-a. XRD patterns of the starting bentonite and fully ion-exchanged NaMt and CuMt

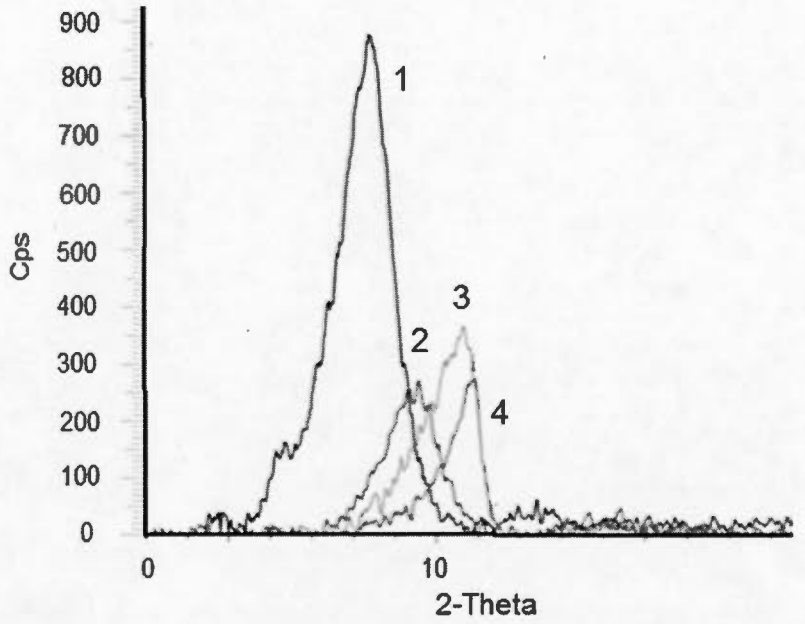


Fig. S2-b. Closeup on low angle XRD patterns of partially ion-exchanged samples: 1. NaFeMt; 2. Bentonite; 3. Partially ion-exchanged bentonite into NaMt; 4. Fully ion-exchanged NaMt

Comments to the XRD patterns:

The 001 reflexion is a special feature of a lamellar mineral, which is montmorillonite in the present case. Sharp 001 xrd line is usually obtained after full ion-exchange into homo-ionic form, and indicates a fairly ordered structure with perfectly parallel arrangement of the clay lamellae. Partial ion-exchange produces broad 001 xrd reflexion, as a result of the presence of cations that differ in size and hydration grade (number of surrounding water molecules per cation). The position (Value of 2-Theta) is a precise indicator of the interlayer spacing, taking into account the 4.2-4.3 angstroms lamella thickness.

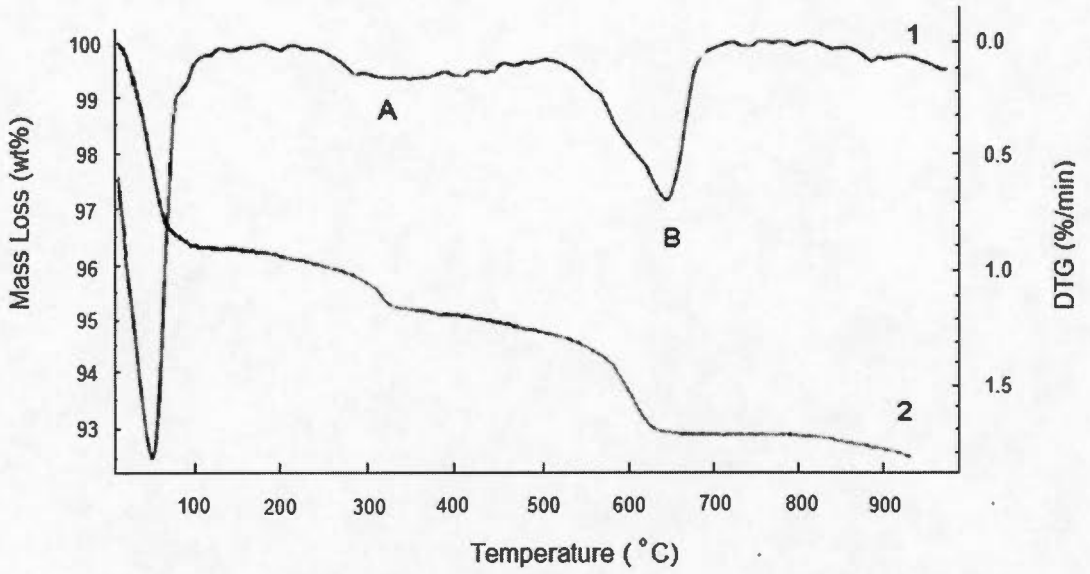


Fig. S3. DTG (1) and TG (2) patterns in air stream of uncalcined NaMt

Thermal programmed desorption measurements (TPD) of the CO_2 retention capacities (*CRC*) were performed after contacting each sample (40 mg, particle size of 0.05 - 0.1 mm) with dry CO_2 (1.5-500 mL) at 20°C, under a nitrogen stream (15 $mL.min^{-1}$). After saturation, the non-adsorbed CO_2 excess was evacuated by 15 $mL.min^{-1}$ of nitrogen stream until no CO_2 was detected.

APPENDIX C

OZONATION PROCEDURE

Ozonation was carried out at ambient temperature and pressure in a 4 cm x 30 cm cylindrical glass reactors containing $3x10^{-4}$ M solutions of various organic substrates. Phenol (99.5% purity, Merck), chlorobenzene (99.5% purity, Anachemia Canada Inc.), benzoic acid (98% purity, Fisher Scientific), 4-nitrobenzoic acid (97% purity), 3-hydroxybenzaldehyde (98% purity) and 4-nitrophenol (98 % purity) were employed as probes to investigate the ozonation of sulfamethoxazole (99% purity). Some of these compounds were supplied by Aldrich Chemical Company Inc. The amount of catalyst (1.91 $g.L^{-1}$) and pHs used (2.88) were similar to those already optimized for oxalic acid (Shahidi *et al.*, 2014). When necessary, the pH level was adjusted using concentrated hydrochloric acid (36.5% purity) supplied by Caledon Ltd. and sodium hydroxide pills (95% purity, Anachemia Canada Inc.). An Accumet 15 pH meter was employed for periodical pH measurements during ozonation. Various ion-exchanged montmorillonites, namely Co(II)-Mt, Ni(II)-Mt, Cu(II)-Mt and Fe(II)-Mt, prepared by similar procedures, were tested as powder catalysts with an average particle size of 0.1-0.2 mm. Since Fe(II)-Mt showed highest activity under various conditions, deeper insights were achieved with were achieved with various iron contents.

After given ozonation times, the catalyst was separated centrifugation, and the supernatant was analyzed by UV-Visible spectrophotometry (Cary 1 E instrument)

and a chemical oxygen demand method (COD), using concentrated sulphuric acid (98% purity, Caledon Ltd.), potassium dichromate 99.5%, iron(II) ammonium sulphate 99.5%, silver sulphate 99.5% and mercury(II) sulphate 99.5% (Anachemia Canada Inc.). Accurate COD measurements required previous determination of optimum concentration ranges of all organic substrates using a linear calibration curves, like that plotted for phenol taken as the reference (Fig. S4). Total COD removal is assumed to correspond to a complete mineralization of the organic compounds.

APPENDIX D

LIQUID CHROMATOGRAPHY – MASS SPECTROMETRY ANALYSIS (LC-MS)

LC-MS analyses were run using two LC–ESI–MS systems: ***i.*** In system 1, the HPLC instrument was connected to an Agilent 6410 quadrupole (triple Q) mass spectrometer using electrospray ionization in positive ESI mode with the following conditions capillary voltage: 3000 V, nebulizer pressure: 60 Psi, gas temperature 300°C, drying gas: 5 $L.min^{-1}$ and a dwell time of 75 micro-seconds. The data were processed using the Mass Hunter software; ***ii.*** In system 2, the same aforementioned column was used. An identical HPLC instrument under the same conditions listed above was connected to another mass spectrometer consisting of an Agilent 6210 electrospray ionization-time-of flight analyzer (ESI–TOF) in positive ESI mode, at a capillary voltage of 4000 V, nebulizer pressure of 35 Psi, a gas temperature of 350 ^0C, drying gas flow: 11.5 $L.min^{-1}$ and voltages of 125 V and 60 V for the fragmentor and skimmer, respectively. The technical error and mass resolving power of the time-of-flight mass spectrometer in terms of mass accuracy was 5 ppm. A reserpine solution with m/z 609.2807 for $[M+H]^+$ ion was used as an internal standard for mass reference. When available, commercial reference compounds were used to compare the corresponding retention times.

Tandem mass technique MS–MS in multiple reaction monitoring (MRM) mode and exact mass measurements via (ESI–TOF) were applied for identifying most phenolic compounds. Multiple reactions monitoring (MRM) is a selective and sensitive LC–

MS/MS technique in which each ionized compound gives a distinct precursor-to-product ion transition. Furthermore, peaks containing co-eluting compounds were resolved by monitoring for specific precursor-to-product ion transitions (Moheb *et al.*, 2011; Chiwosha *et al.*, 2003; Pang *et al.*, 2009; Segarra *et al.*, 2006). Another analysis using the same conditions was conducted on another instrument (ESI–TOF) in order to confirm the exact masses and empirical formulae of each of the identified structures. For each intermediates, MRM acquisition was carried out by monitoring transitions of the combination of the parent ion mass and the fragment ions. Using these protocols allowed the identification of intermediate compounds in the ozonized pollutant solutions. The mass axis was calibrated over the m/z range of 50-1000 and MS spectra were acquired over the m/z 50-500 range at a scan rate of 0.5 seconds per spectrum. The data recorded were processed with Agilent Mass Hunter Workstation software. The LC–TOF system was equipped with Agilent software that allowed calculating and generating the molecular formula of each compound according to its mass spectrum obtained during analysis, whereas the triple quadrupole MS/MS system was used to confirm the product ions.

COD calibration curves were plotted for all the organic substrates investigated herein, but for the sake of brevity only that established for phenol is presented below (Fig. S4).

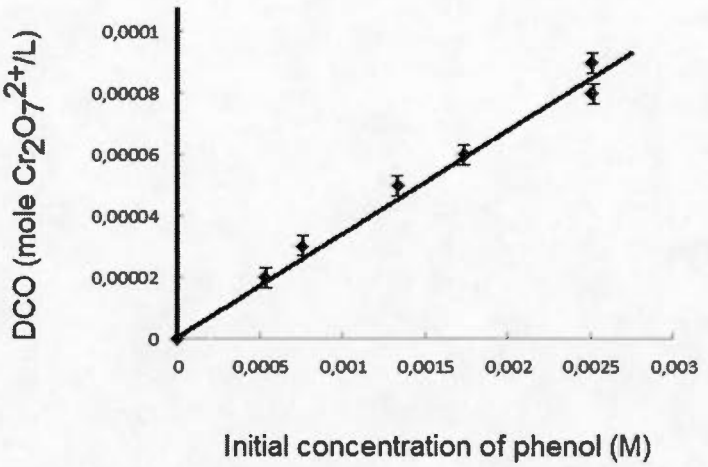


Fig. S4. COD calibration plot for phenol at initial pH adjusted at 2.88. This concentration range plotted for phenol was taken as a reference for COD assessments for all other organic substrates, because of the constant measurement error, which did not exceed 1%.

APPENDIX E

EFFECT OF CATALYST ON THE DEPLETION OF THE RELATIVE ABSORBANCE

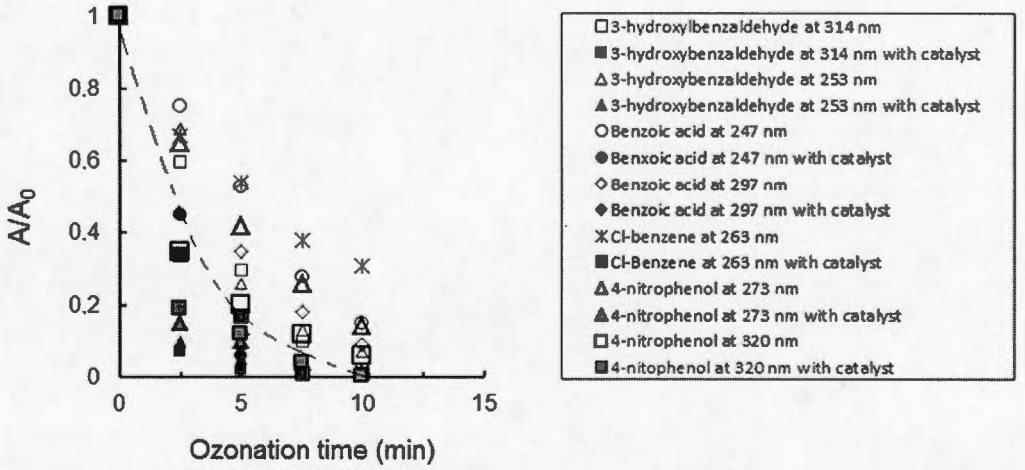


Fig. S5. Evolution in time of the relative absorbance of the main UV-Vis band before and after Fe(II)Mt addition (1.91 $g.L^{-1}$) at initial pH=2.88. $C_{initial}$= 3.10^{-4} M; ozone feed: 6 $mg.min^{-1}$. The dashed line separates the ozonation experiments with (dark symbols) and without catalyst (white symbols).

APPENDIX F

COD EVOLUTION IN TIME FOR ALL ORGANIC SUBSTRATES

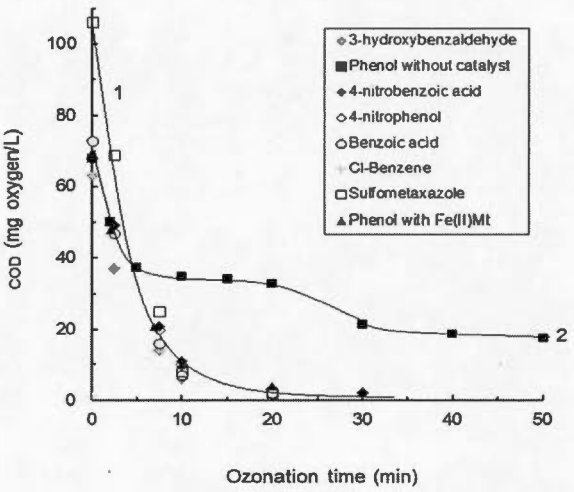


Fig. S6. Evolution in time of the chemical oxygen demand. Fe(II)Mt amount: 1.91 $g.L^{-1}$; initial pH=2.88; $C_{initial}$= 3.10^{-4} M; ozone feed: 6 $mg.min^{-1}$.

APPENDIX G

COMPARISON OF THE REQUIRED TIME FOR DECOMPOSITION OF THE ORGANIC SUBSTRATES

Table S2. Required time for total depletion of absorbance at λ_{max} and COD via Fe(II)Mt- catalyzed ozonation of different organic substrates

Feature measured		Required time for total depletion (min)[a]				Final pH	
Catalyst		None		Fe(II)Mt		None	Fe(II)Mt
Organic substrate	λ_{max} (nm)	Absorbance[b]	COD[c]	Absorbance[b]	COD[c]		
phenol	269	30	> 100	7.5	30	3.17	3.32
Chlorobenzene	263	40	> 100	7.5	20	3.19	3.31
Benzoic acid	247	30	> 150	7.5	20	3.17	3.32
	297	20	> 180				
4-Nitrobenzoic	273	40	> 100	9	30	3.24	3.29
3-Hydroxybenzaldehyde	253	20	> 150	7.5	20	3.18	3.29
	314		> 150				
4-Nitrophenol	320	30	> 180	8.5	30	3.22	3.38

[a] The ozonation tests were carried out using a 6 mg/min ozone stream bubbling in 20 mL samples of different organic substrates (3.10^{-4} M) at pH adjusted to 2.88, in the presence of with Fe(II)Mt (1.91 $g.L^{-1}$), if any;

[b] Required time (in minutes) for total depletion of the absorbance of the main UV-Vis band for each organic substrate;

[c] Required time (in minutes) for complete COD removal for each organic substrate.

Table S3. Acid-base properties of some ion-exchanged montmorillonite*

Sample	Acidity (mmol desorbed $NH_3.g^{-1}$)	Acid site distribution**				Basicity (mmol desorbed $CO_2.g^{-1}$)	Basic site distribution**			
		Weak	Medium	Strong	Very strong		Very weak	Weak	Medium	Strong
NaMt	0.35	50	40	10	0	1.55	30	35	20	15
Fe(II)Mt	2.10	2	30	25	43	0.55	45	28	20	7
Co(II)Mt	1.35	15	39	34	12	0.5	40	35	10	15

* Data obtained in correlation with those already published in Azzouz *et al.*, Thermochimica Acta, 2006, 449, 27-34.
**The strength distribution was assessed by peak deconvolution in the corresponding TPD profiles between 20 and 450°C.

APPENDIX H

EFFECT OF THE EXCHANGEABLE CATIONS ON THE OZONATION OF SULFAMETHOXAZOLE

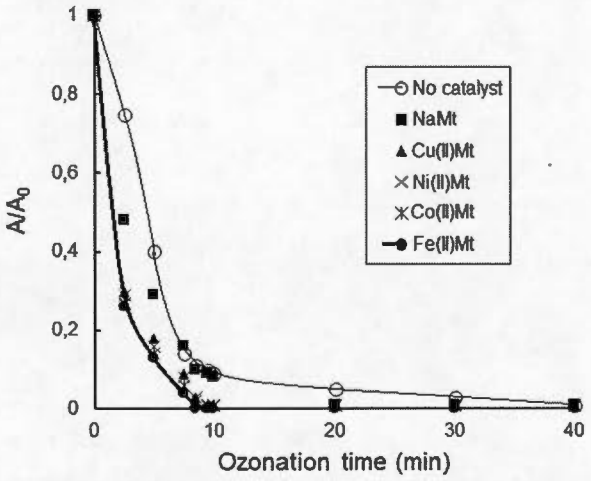


Fig. S7. Effect of the exchangeable cation on the relative absorbance at 266 nm in the ozonation of sulfamethoxazole . Catalyst amount:1.91 $g.L^{-1}$; initial pH=2.88; $C_{initial}= 3.10^{-4}$ M; ozone feed: 6 $mg.min^{-1}$.

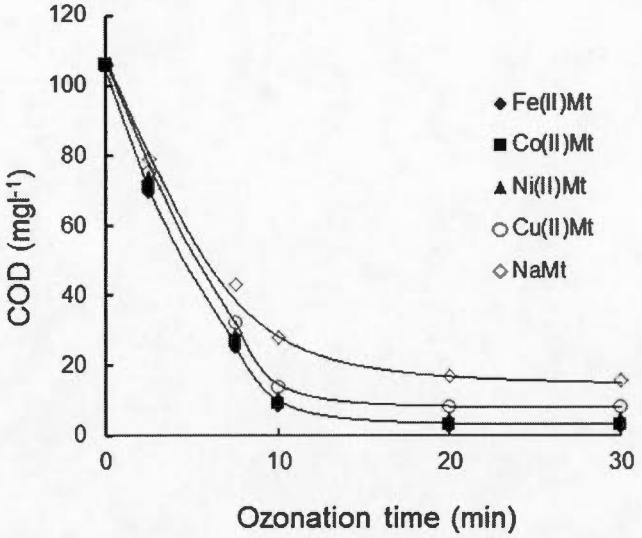


Fig. S8. Effect of the exchangeable cation on the COD in the ozonation of sulfamethoxazole . Catalyst amount:1.91g.L^{-1}; initial pH=2.88; $C_{initial}$= 3.10^{-4}M; ozone feed: 6 $mg.min^{-1}$.

APPENDIX I

EFFECT OF IRON CONTENT ON THE SULFAMETHOXAZOLE DECOMPOSITION

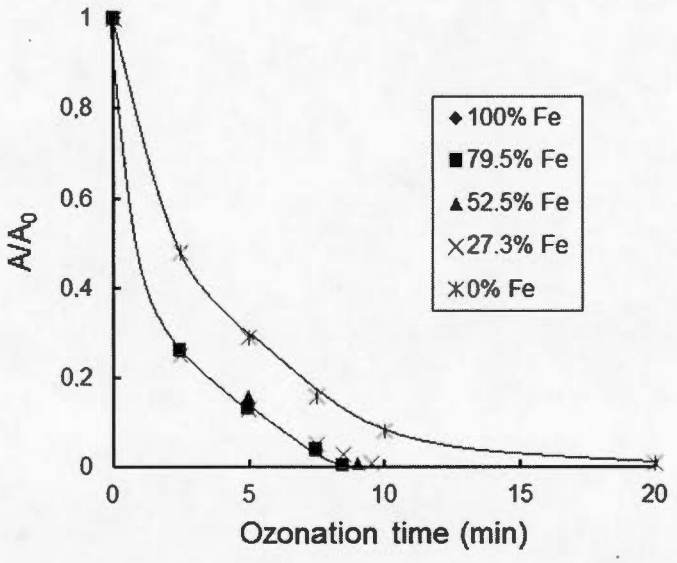


Fig. S9. Effect of the iron content on the relative absorbance at 266 nm in the ozonation of sulfamethoxazole . Fe(II)Mt amount:1.91g.L^{-1}; initial pH=2.88; $C_{initial}$= 3.10^{-4}M; ozone feed: 6 mg.min^{-1}. Error in Fe content: 3%.

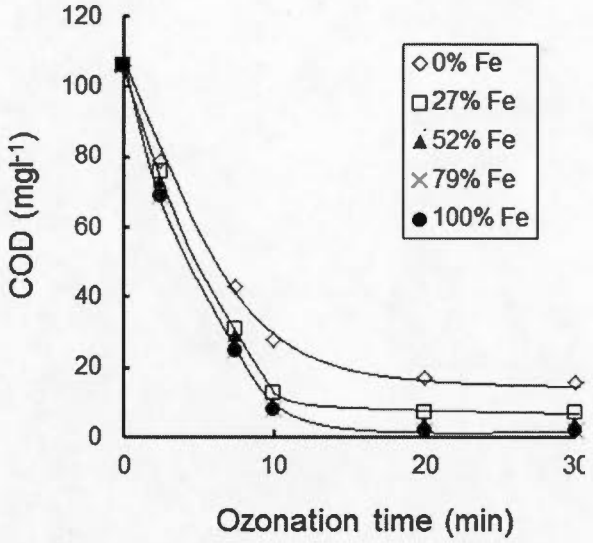


Fig. S10. Effect of the iron content on the COD in the ozonation of sulfamethoxazole . Fe(II)Mt amount:1.91 $g.L^{-1}$; initial pH=2.88; $C_{initial}$= 3.10^{-4} M; ozone feed: 6 $mg.min^{-1}$. Error in Fe content: 3%.

Table S4. Required time for sulfamethoxazole ozonation with Fe(II)Mt[1] at different iron contents

Ion exchange yield (%)[2]	Required time for total depletion (min.)		COD removal yield (%)	Final pH
	Absorbance at λ_{max} (266 nm)	COD		
No catalyst	40	-	-	3.10
0	20	30	84	3.12
27.3	9.5	20	93	3.18
52.5	9.0	20	96	3.24
79.5	8.0	20	98	3.30
100	8.0	20	98	3.32

[1] Fe(II)Mt catalyst amount in all experiments: 1.91 g/L;
[2] Error in Fe content: 3%.

APPENDIX J

MASS SPECTROMETRY FOR INTERMEDIATE IDENTIFICATION

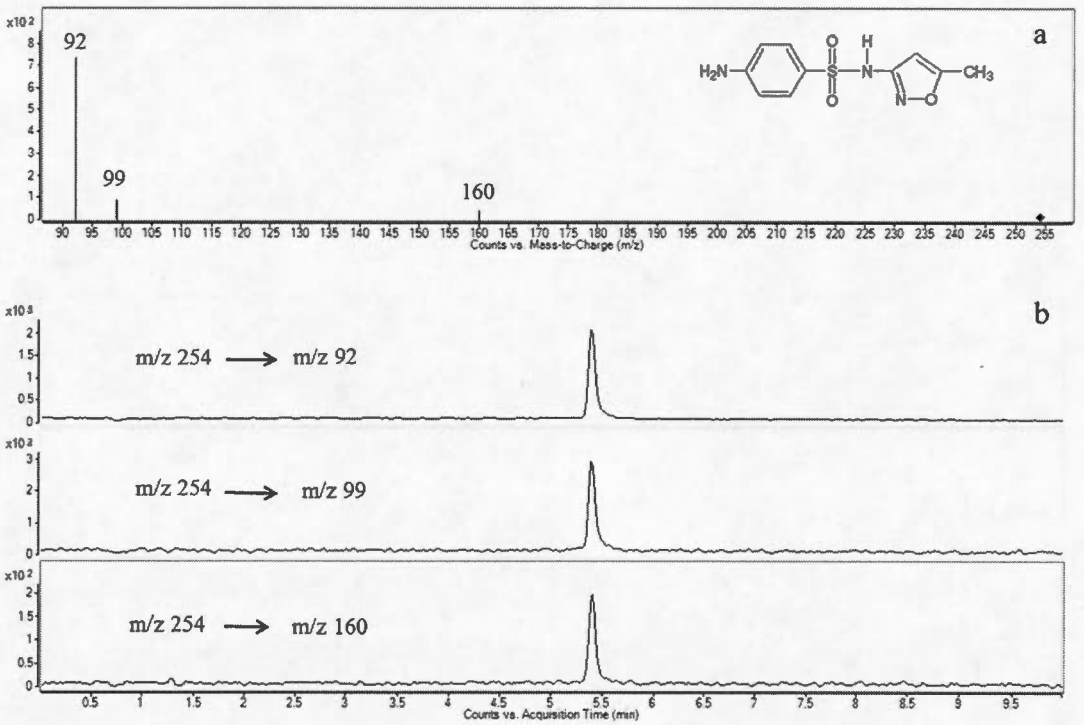


Fig. S11. (a) Identification of SMX, MS–MS of the compound at m/z 254 $[M+H]^+$ showing 92, 99 and 160 as major product ions; (b) MRM signal for SMX at 254, 92, 99 and 160 ions.

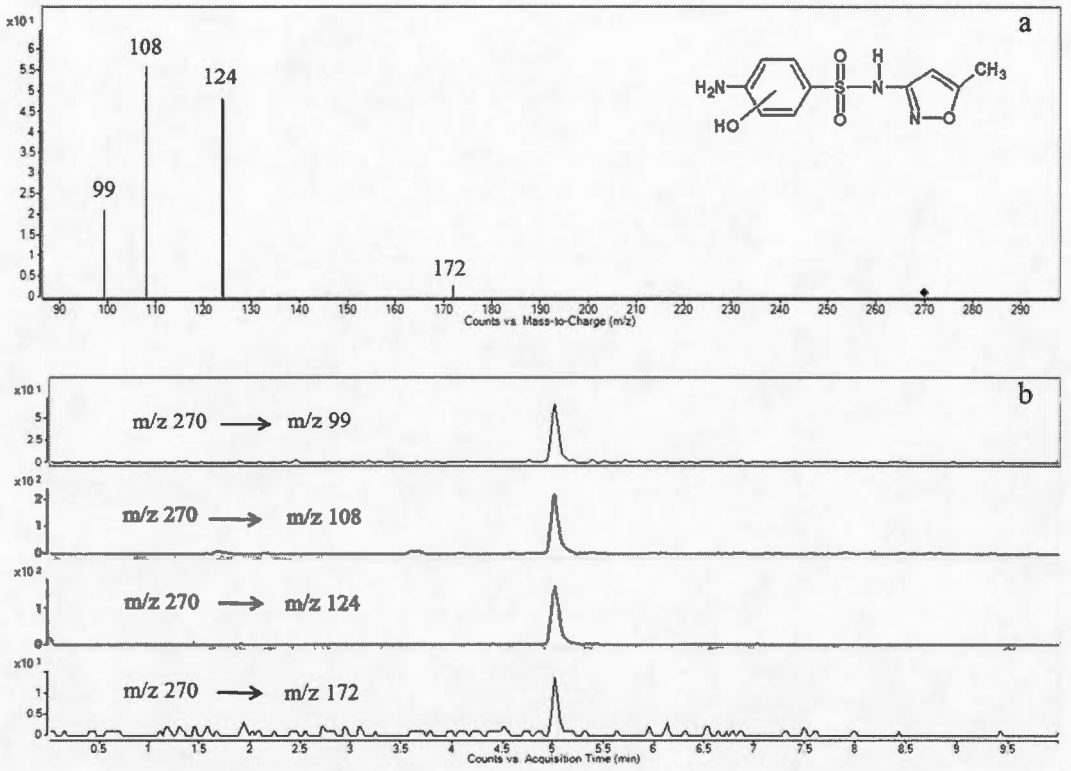


Fig. S12. (a) Identification of intermediate 1: MS–MS of the compound at m/z 270 $[M+H]^+$ showing 99, 108, 124 and 172 as major product ions; (b) MRM signals for intermediate **1** at 270, 99, 108, 124 and 172 ions.

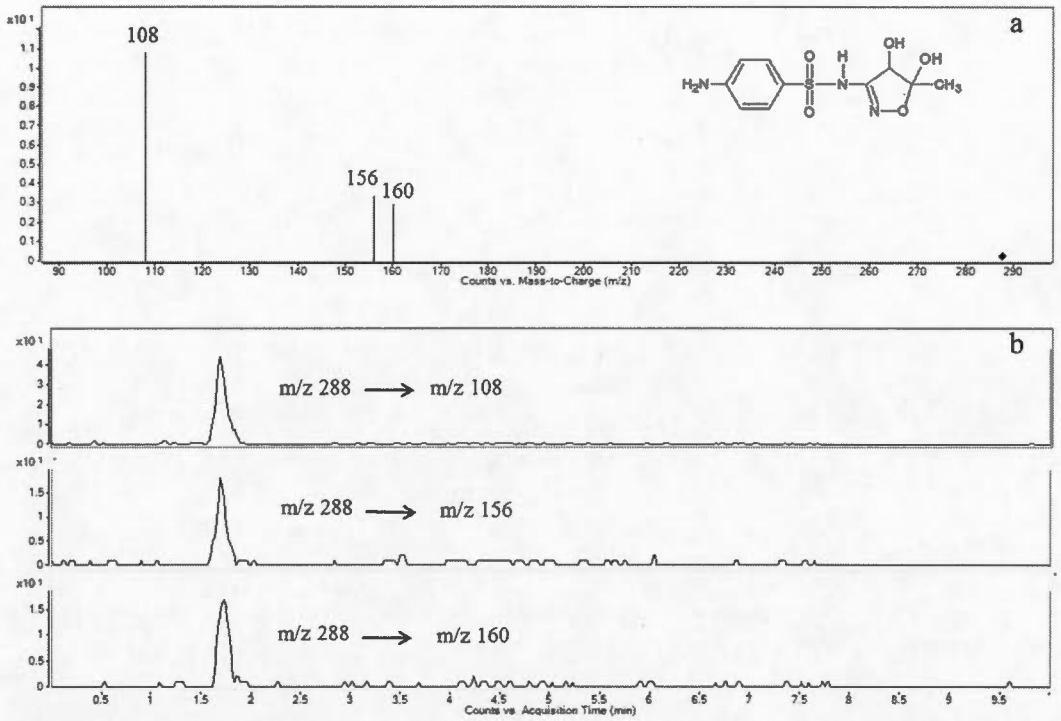


Fig. S13. (a) Identification of intermediate 2, MS–MS of the compound at m/z 288 $[M+H]^+$ showing 108, 156 and 160 as major product ions; (b) MRM signal for intermediate 2 at 288, 108, 156 and 160 ions.

Intermediates 3 and 4 have a same m/z value but different retention times due to different structural formulae. In fact, the derivative ion of m/z 174 proposes a nitric oxide group on benzene ring for intermediate 3 while that of m/z 122 involves a nitrogen dioxide group on the same benzene ring for intermediate 4, both arising from the oxidation of the amine group on the benzene ring.

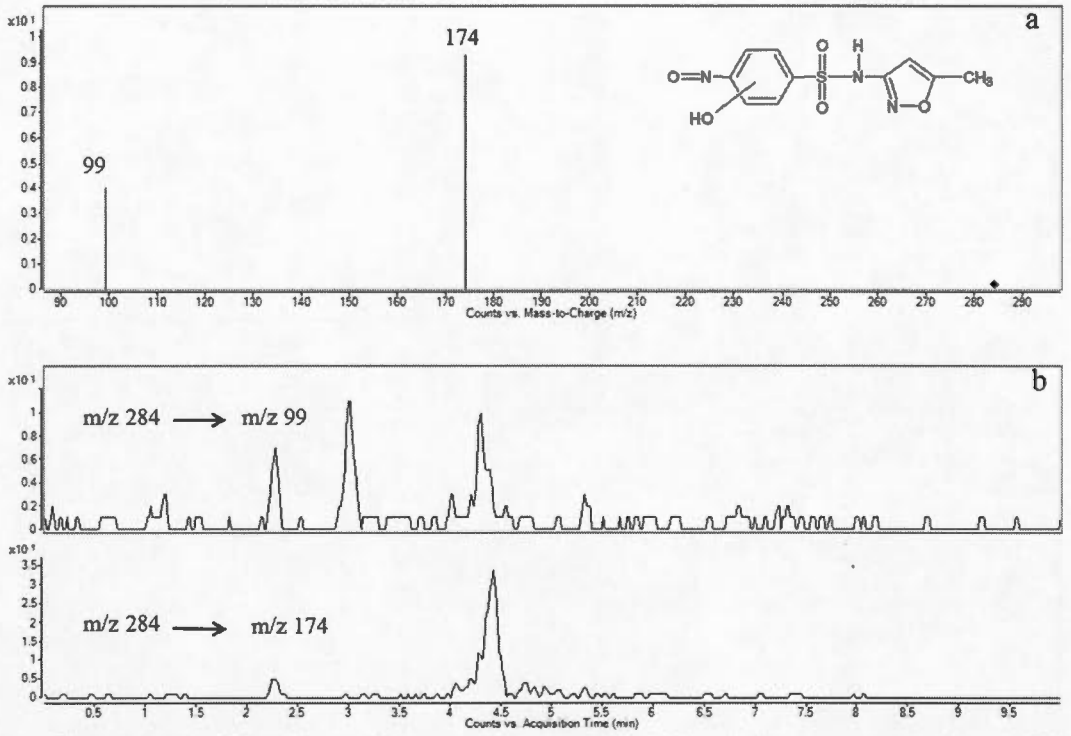


Fig. S14. (a) Identification of intermediate 3, MS–MS of the compound at m/z 284 $[M+H]^+$ showing 99 and 174 as major product ions; (b) MRM signal for intermediate 3 at 284, 99 and 174 ions.

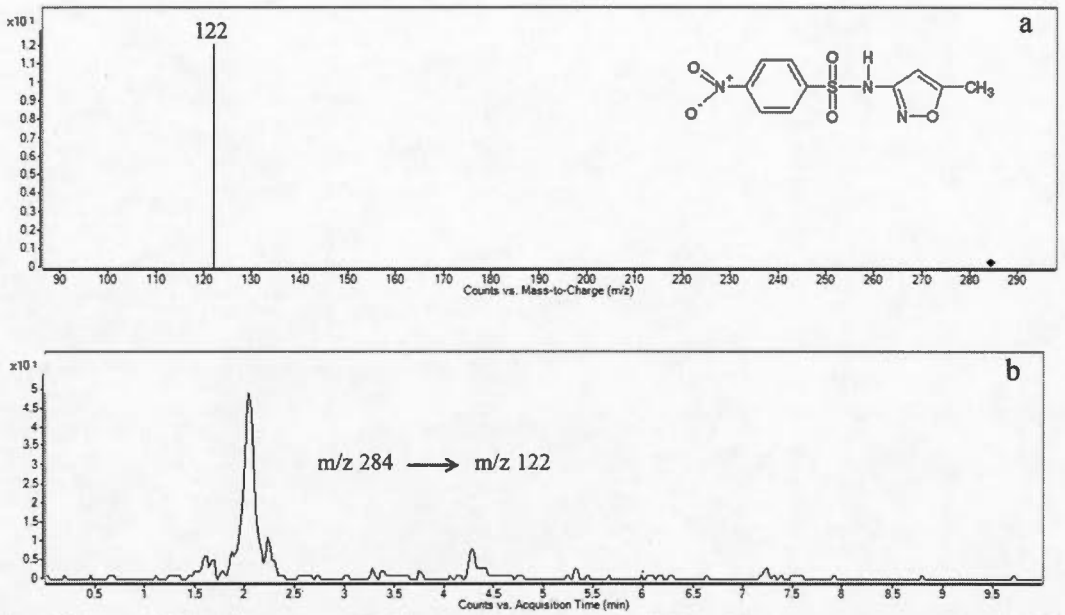


Fig. S15. (a) Identification of intermediate 4, MS–MS of the compound at m/z 284 $[M+H]^+$ showing 122 as a major product ion; (b) MRM signals for intermediate 4 at 284 and 122 ions.

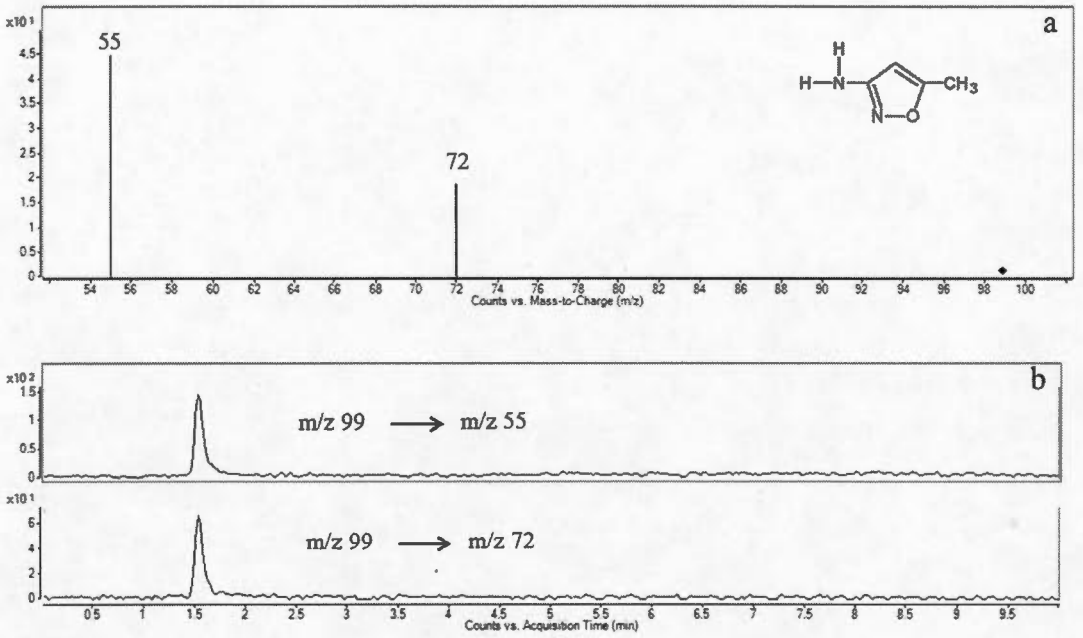


Fig. S16. (a) Identification of intermediate 5, MS–MS of the compound at m/z 99 $[M+H]^+$ showing 72 and 55 as major product ions; (b) MRM signals for intermediate 5 at 99, 72, 55 ions.

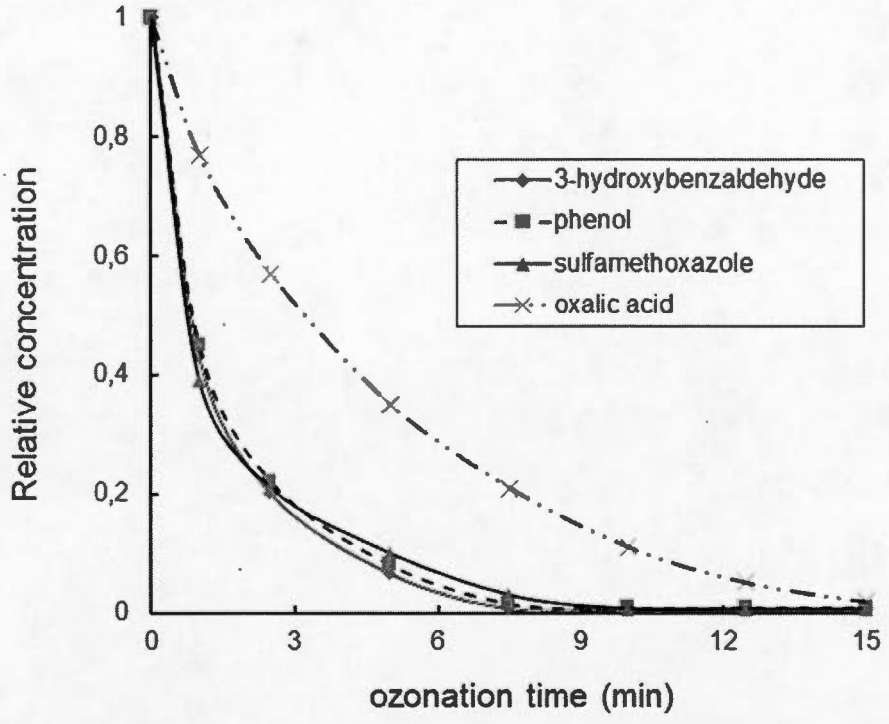


Fig. S17. Evolution in time of the relative concentration as determined by LC-MS (C/C_0). Fe(II)Mt amount:1.91 $g.L^{-1}$; initial pH=2.88; $C_{initial}$= 3.10^{-4} M; ozone feed: 6 $mg.min^{-1}$.

Table S5. Intermediate identification by LC-ESI (+) TOF for sulfamethoxazole catalytic ozonation

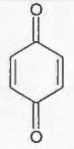
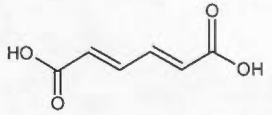
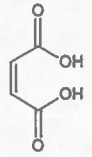
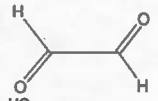
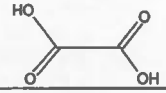
Intermediate	Retention time (min.)	Formula	Measured mass	Discrepancy from theoretical mass (ppm)	Structure
Benzoquinone	3.82	$C_6H_4O_2$	108.0219	-1.41	
Muconic acid	4.41	$C_6H_6O_4$	142.0265	3.74	
Maleic acid	1.25	$C_4H_4O_4$	116.0113	3.29	
Glyoxal	0.891	$C_2H_2O_2$	58.0057	4.22	
Oxalic acid	0.632	$C_2H_2O_4$	89.9952	5.09	

Table S6. Intermediate identification by LC-ESI (+) TOF for 3-hydroxybenzaldehyde catalytic ozonation

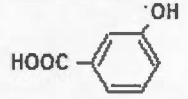
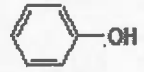
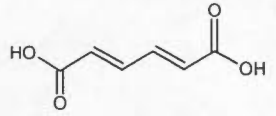
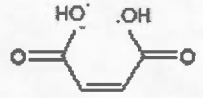
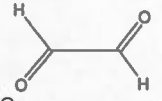
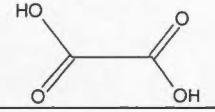
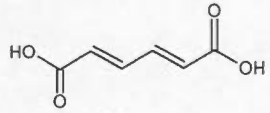
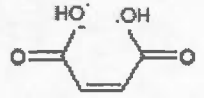
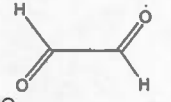
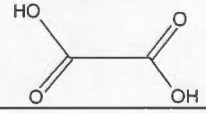
Intermediate	Retention time (min.)	Formula	Measured mass	Discrepancy from theoretical mass (ppm)	Structure
3-Hydroxy-benzoic acid	4.32	$C_7H_6O_3$	138.0316	-0.45	
Phenol	5.553	C_6H_6O	94.0418	-1.1	
Benzoquinone	3.82	$C_6H_4O_2$	108.0211	-1.67	
Muconic acid	4.51	$C_6H_6O_4$	142.0267	0.49	
Maleic acid	1.29	$C_4H_4O_4$	116.0111	1.63	
Glyoxal	1.01	$C_2H_2O_2$	58.0053	-2.64	
Oxalic acid	0.622	$C_2H_2O_4$	89.9949	-4.57	

Table S7. Intermediate identification by LC-ESI (+) TOF for phenol catalytic ozonation

Intermediate	Retention time (min.)	Formula	Measured mass	Discrepancy from theoretical mass (ppm)	Structure
Benzoquinone	3.83	$C_6H_4O_2$	108.0210	-0.22	
Muconic acid	4.40	$C_6H_6O_4$	142.0261	3.79	
Maleic acid	1.058	$C_4H_4O_4$	116.0121	2.58	
Glyoxal	1.01	$C_2H_2O_2$	58.0055	2.12	
Oxalic acid	0.603	$C_2H_2O_4$	89.9954	4.47	

APPENDIX K

EQUATIONS USED IN THE KINETIC STUDY OF THE OZONATION PROCESSES

1. Kinetic models for the disappearance of the parent organic substrates

1.1. First order model:

First order model for the relative absorbance $\Rightarrow A_{r.} = \left(A / A_o \right)$

$$-\frac{\Delta A_{r.}}{\Delta t} = k \text{ x } A_{r.Med.}$$

$$A_{r.Med.} = (A_{r.1} + A_{r.2})/2$$

Plotting $-\frac{\Delta A_{r.}}{\Delta t} = F(A_{r.Med.})$ provides the value of the rate constant as the line slope.

First order model for the COD $\Rightarrow COD_{r.} = \left(COD / COD_o \right)$

$$-\frac{\Delta COD_{r.}}{\Delta t} = k \text{ x } COD_{r.Med.}$$

$$COD_{r.Med.} = (COD_{r.1} + COD_{r.2})/2$$

Plotting $-\frac{\Delta COD_{r.}}{\Delta t} = F(COD_{r.Med.})$ provides the value of the rate constant as the line slope.

1.2. n- order model:

n - order model for the relative absorbance $\Rightarrow A_{r.} = \left(A / A_o \right)$

$$-\frac{\Delta A_{r.}}{\Delta t} = k \text{ x } (A_{r.Med.})^n \quad , A_{r.Med.} = (A_{r.1} + A_{r.2})/2 \Rightarrow \quad Ln\left(-\frac{\Delta A_{r.}}{\Delta t}\right) = Ln(k) + n \text{ x } Ln(A_{r.Med.})$$

Plotting $Ln\left(-\frac{\Delta A_{r.}}{\Delta t}\right) = F(Ln(A_{r.Med.}))$ provides:

1) the value of the reaction order as the line slope
2) the value of the rate constant as the Y-intercept

n - order model for the COD $\Rightarrow COD_{r.} = \left(COD / COD_o \right)$

$$-\frac{\Delta COD_{r.}}{\Delta t} = k \text{ x } (COD_{r.Med.})^n \quad , COD_{r.Med.} = (COD_{r.1} + COD_{r.2})/2$$

$$\Rightarrow \quad Ln\left(-\frac{\Delta COD_{r.}}{\Delta t}\right) = Ln(k) + n \text{ x } Ln(COD_{r.Med.})$$

Plotting $Ln\left(-\frac{\Delta COD_{r.}}{\Delta t}\right) = F\left(Ln(COD_{r.Med.})\right)$ provides:

1) the value of the reaction order as the line slope
2) the value of the rate constant as the Y-intercept

2. Kinetic models for the formation of the intermediates

2.1. First order model:

First order model for the production yield $\Rightarrow X = \left({Count_2 - Count_1}/{Count_{Med}} \right)$

$Count_{Med} = (Count_2 + Count_1)/2$

$$\frac{\Delta X}{\Delta t} = k \text{ x } (1 - X_{Med})$$

Plotting $\frac{\Delta X}{\Delta t} = F(1 - X_{Med})$ provides the value of the rate constant as the line slope.

2.2. n- order model:

n - order model for the production yield $\Rightarrow X = \left({Count_2 - Count_1}/{Count_{Med}} \right)$

$Count_{Med} = (Count_2 + Count_1)/2$

$$\frac{\Delta X}{\Delta t} = k \text{ x } (1 - X_{Med})^n \quad \Rightarrow \quad Ln\left(\frac{\Delta X}{\Delta t}\right) = Ln(k) + n \text{ x } Ln(1 - X_{Med})$$

Plotting $Ln\left(\frac{\Delta X}{\Delta t}\right) = F\left(Ln(1 - X_{Med})\right)$ provides:

1) the value of the reaction order as the line slope
2) the value of the rate constant as the Y-intercept

APPENDIX L

KINETIC STUDY FOR THE OZONATION PROCESSES

Hypotheses: The kinetic study was achieved using both the COD and spectrophotometric measurements for assessing respectively the global rate constant for the ozonation process as a whole and specific rate constant for individual reaction. For this purpose, three hypotheses were taken into account, namely: ***1.*** Given the limited solubility of ozone in the aqueous media, the ozone concentration will be regarded as being constant, and a first order kinetic model will be tested for the first 3-5 min of ozonation; ***2.*** As the process evolves in time, for the first 3-5 minutes, the limited ozone solubility will be supposed to generate constant amounts of oxidative species and (or) radicals, if any, regardless to the organic substrates exposed to ozone and its derivatives; ***3.*** The n-order model used will be expected to provide information about possible complex degradation process for a single organic substrate, if any.

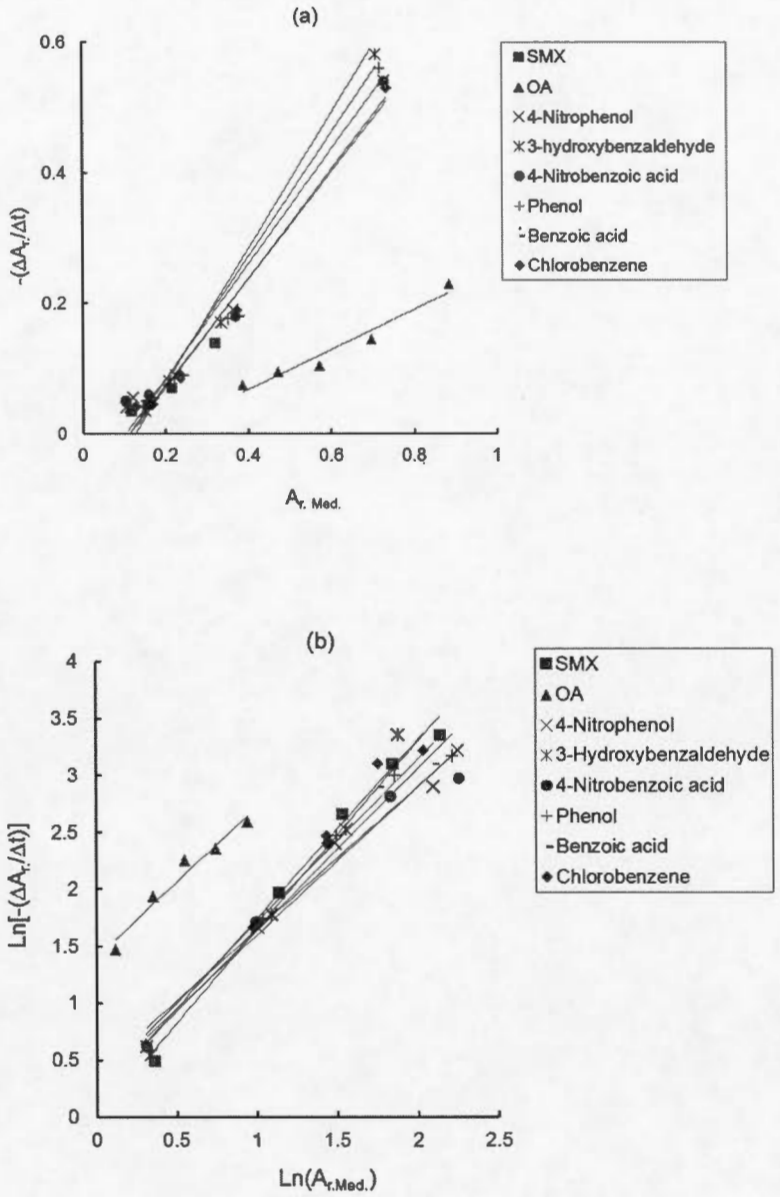


Fig. S18. First-order (a) and n-order (b) models for the depletion in time of the relative absorbance ($A_r=A/A_0$) of the main UV-Vis band; $A_{r.Med.}=(A_{r.1}+A_{r.2})/2$.

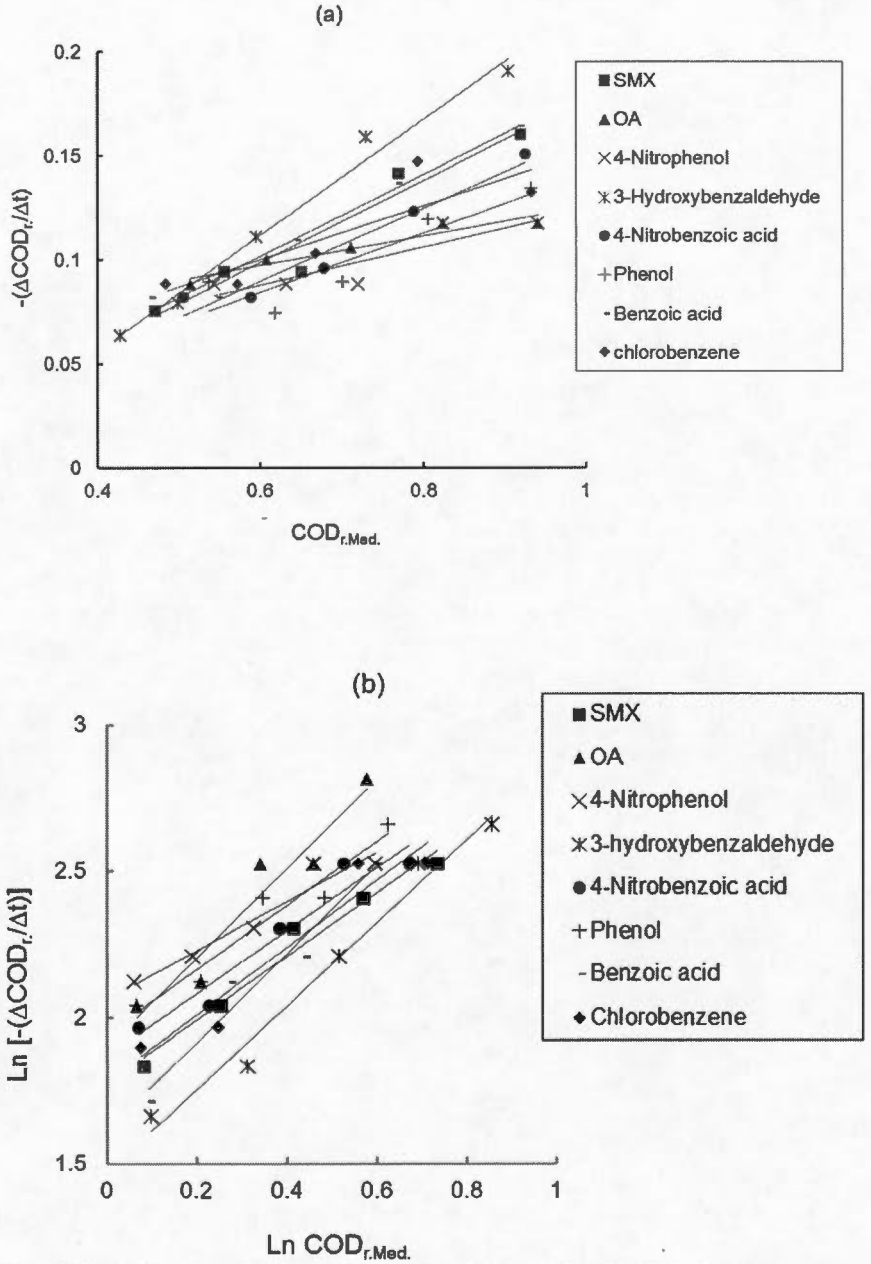


Fig. S19. First-order (a) and n-order (b) model for the depletion in time of COD. $COD_r=COD/COD_0$, $COD_{r.Med.}=(COD_{r.1}+COD_{r.2})/2$.

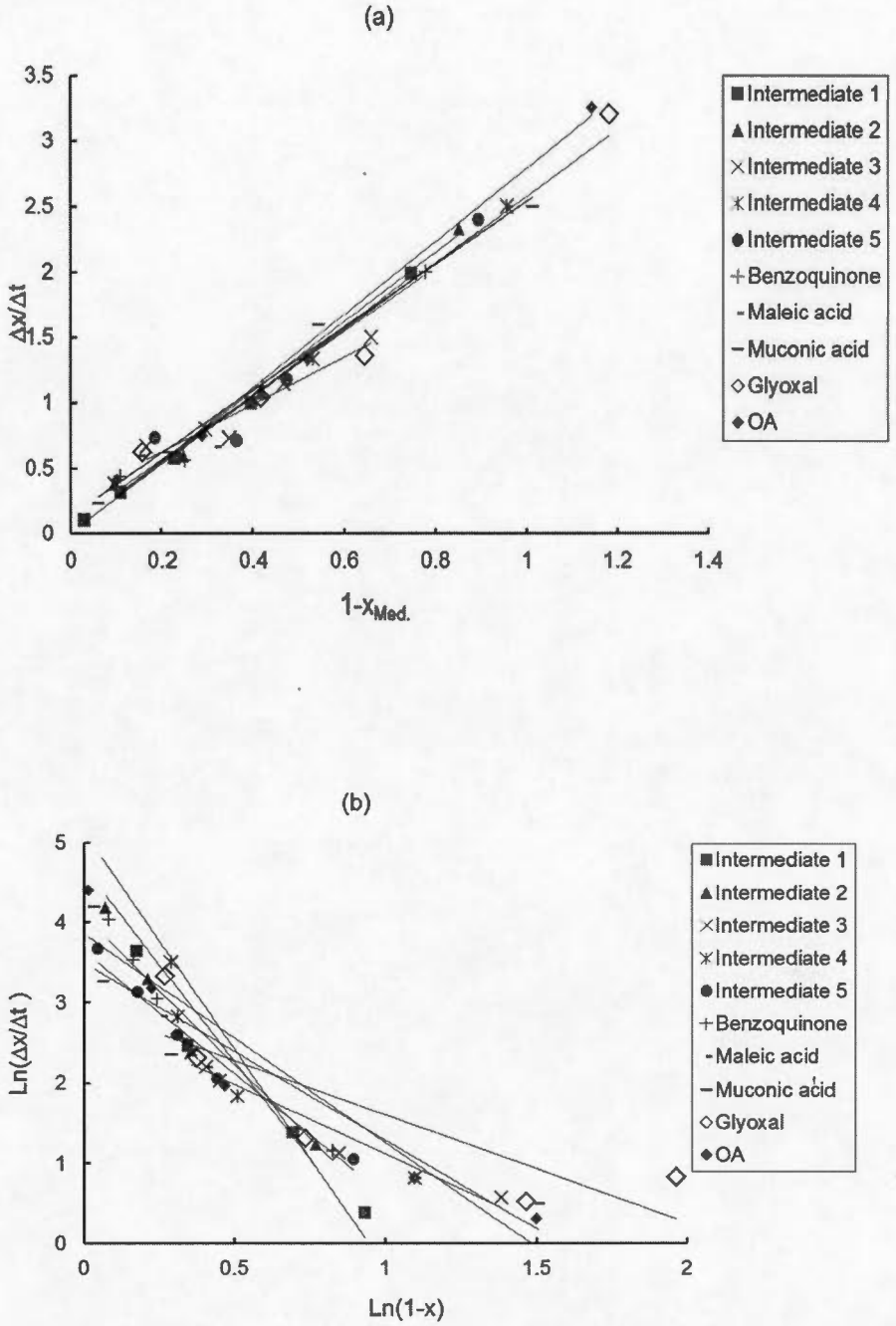


Fig. S20. First-order (a) and n-order (b) model for the formation of intermediates of sulfamethoxazole monitored by HPLC-MS measurements; X is the conversion expressed in terms of molar fraction; $X=(Count_2-Count_1)/Count_{Med.}$, $Count_{Med.}=(Count_1+Count_2)/2$.

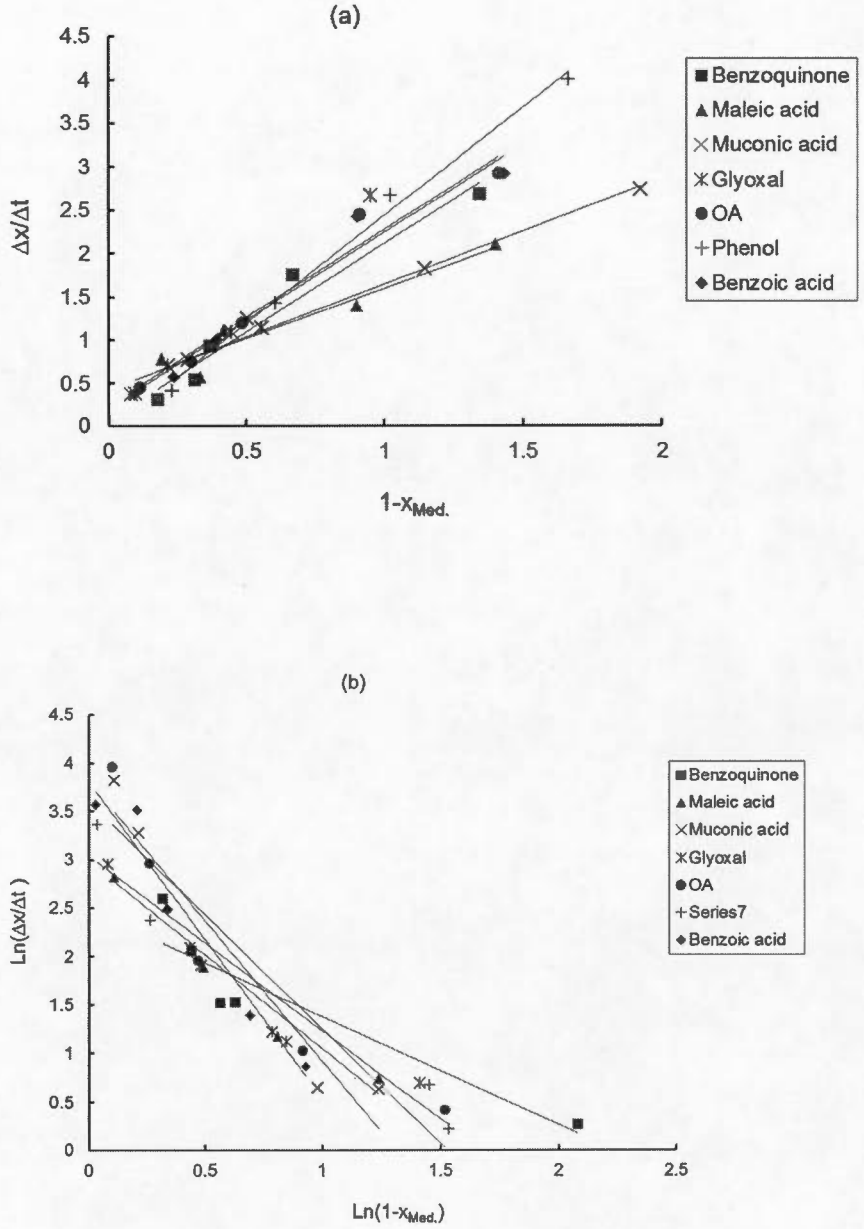


Fig. S21. First-order (a) and n-order (b) model for the formation of intermediates of 3-hydroxybenzaldehyde monitored by HPLC-MS measurements; X is the conversion expressed in terms of molar fraction; $X=(Count_2-Count_1)/Count_{Med.}$, $Count_{Med.}=(Count_1+Count_2)/2$.

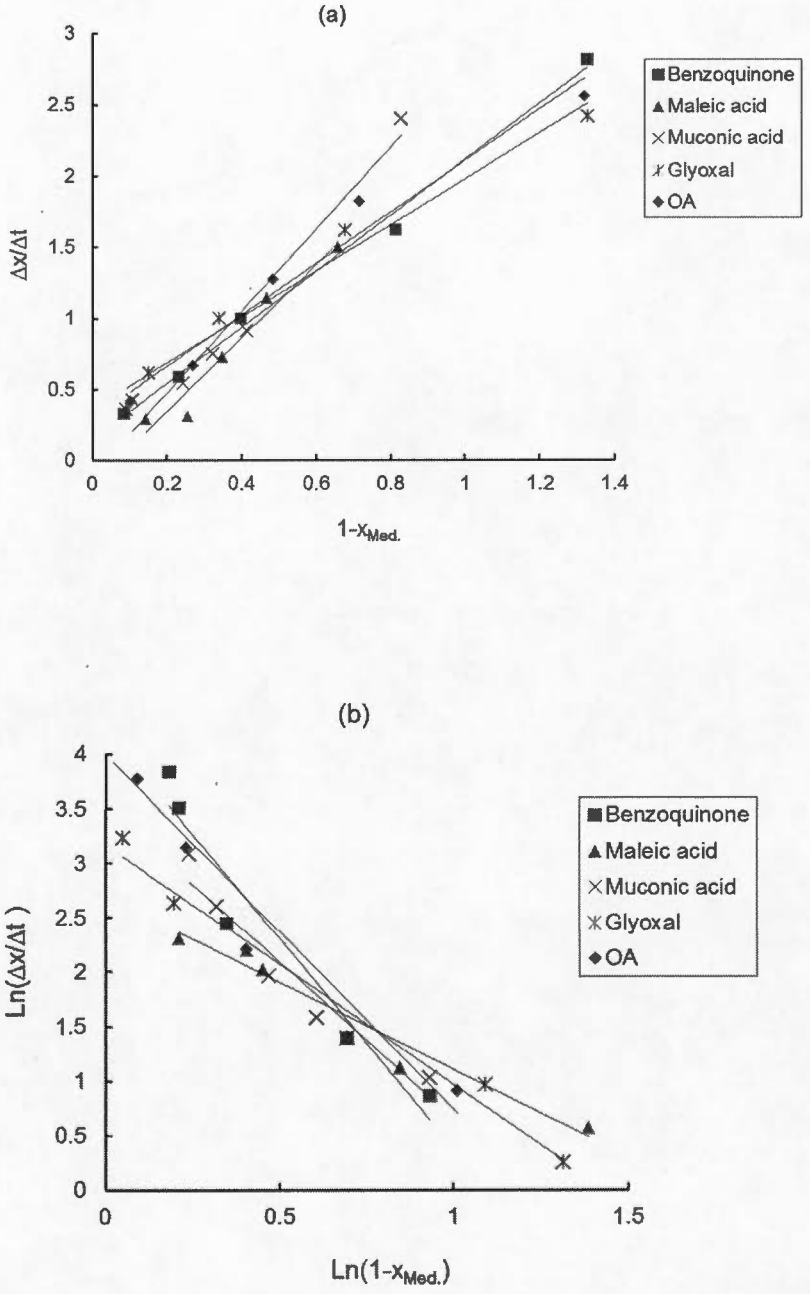


Fig. S22. First-order (left) and n-order (right) model for the formation of intermediates of phenol monitored by HPLC-MS measurements; X is the conversion expressed in terms of molar fraction; $X=(Count_2-Count_1)/Count_{Med.}$, $Count_{Med.}=(Count_1+Count_2)/2$.

APPENDIX M

DESCRIPTION OF COEFFICIENTS OF THE POLYNOMINAL MODELS

Table S8. Description of each type of coefficients of the polynomial models.

Symbol	Description of symbol
a_0	value at (0,0,0)
a_1	Individual effect of initial pH
a_2	Individual effect of ozonation time (min.)
a_3	Individual effect of catalyst amount ($g.L^{-1}$)
a_{11}	Quadratic term representing response-surface convexity of initial pH
a_{22}	Quadratic term representing response-surface convexity of ozonation time
a_{33}	Quadratic term representing response-surface convexity of catalyst amount
a_{12}	Binary interaction between initial pH and ozonation time
a_{13}	Binary interaction between initial pH and catalyst amount
a_{23}	Binary interaction between ozonation time and catalyst amount
a_{123}	Ternary interaction between initial pH, ozonation time and catalyst amount

APPENDIX N

PUBLISHED ARTICLES

Shahidi, D., Roy, R., et Azzouz, A. (2014). Total removal of oxalic acid via synergistic parameter interaction in montmorillonite catalyzed ozonation. *Journal of Environmental Chemical Engineering*, 2, 20-30.

Shahidi, D., Roy, R., et Azzouz, A. (2015). Advances in catalytic oxidation of organic pollutants-Prospects for thorough mineralization by natural clay catalysts, *Applied Catalysis B, Environmental,* 174-175, 277-292.

Shahidi, D., Moheb, A., Abbas, R., Larouk, S., Roy, R., et Azzouz, A. (2015). Total mineralization of sulfamethoxazole and aromatic pollutants through Fe^{2+}-montmorillonite catalyzed ozonation, *Journal of Hazardous Materials*, 298, 338-350.

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Total removal of oxalic acid via synergistic parameter interaction in montmorillonite catalyzed ozonation

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ABSTRACT

Oxalic acid ozonation in water at room temperature produced decomposition yields of 50–100% in the presence of Na^+, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ion-exchanged montmorillonite as catalysts. Among these, Co(II)Mt and Fe(II)Mt displayed the highest performances. The appreciable enhancement of oxalic acid removal as compared to homogenous ozonation and the ozonation yield decay upon heating suggest a significant contribution of adsorption. The initial pH of the reaction mixture, ozonation time and catalyst concentration showed strong influence. A 3^k factorial design with 27 ozonation attempts for each catalyst produced total removal of oxalic acid after 15 min at pH 2.87 with 1.88 g/L of Co(II)Mt, and pH 2.88 with 1.91 g/L of Fe(II)Mt. Because oxalic acid is well known to be a quite refractory intermediate in most oxidation attempts, these results suggest that total mineralization of any hazardous organic pollutants from aqueous media is possible under similar optimum conditions. Higher pH and catalyst amounts were detrimental, presumably due clay compaction, which is supposed to reduce the cation mobility and adsorption contribution. The initial pH was found to act also via synergistic interaction with the other parameters, presumably by enhancing clay exfoliation and adsorption of oxalate anion and ozone.

Introduction

Chemical, petrochemical, pharmaceutical and food industries, along with agriculture and forestry are major sources of organic pollutant in waste-waters [1–3]. Primary treatments are not sufficiently effective because of residual traces of pollutants [4,5]. Complete decomposition of organic pollutants requires powerful oxidative treatments to avoid the persistent presence of refractory short chain intermediates like oxalic acid (OA). The latter is known to display high chemical stability even in the so-called Advanced Oxidation Processes (AOPs). The main issue to be addressed is that the formation of OA is often the final stage in most oxidation methods [6–9]. Besides, OA is a hazardous compound [10], and shows even more toxicity than most parent pollutants [11].

Notwithstanding that some plants like rhubarb and sorrel contain OA, the latter is recognized as being quite poisonous to the kidneys (nephrotoxic), more particularly when present in drinking water. OA precipitation in the presence of calcium produces kidney stones, which contain calcium oxalate in a proportion of 80%. OA may even be fatal around a median lethal dose (LD50) of 375–380 mg/kg body weight for humans [12–16]. In human and animal metabolism, OA may also form from excessive use of vitamin C, which is readily oxidized owing to its powerful antioxidizing capacity. This often results in gut lining irritation, rheumatoid arthritis, certain forms of chronic vulvar pains (vulvodynia) and other diseases. However, being quite harmless in low doses, OA is rather regarded as being a precise indicator of incomplete oxidation of organic matter. For this reason, total mineralization of organic pollutants into carbon dioxide (CO_2) without generating any traces of OA or any other short chain compounds has become an essential requirement for effective oxidative water treatments.

So far, attempts to OA oxidative mineralization into CO_2 have received fairly good attention in the published literature, and many advances have been made in this regard [9]. Photocatalysis and photoelectrocatalysis have long been considered promising approaches, but the incomplete decomposition of organic pollutants and high operating costs were still major obstacles for commercial applications [1,3]. AOPs result from continuous improvements of conventional oxidative methods [2]. One of these, namely ozonation, more particularly at elevated pH, has focused interest. Nonetheless, no prospects can be envisaged as long as the issues related to the low solubility of ozone in the liquid media and its weak reactivity as compared to radical species still remain to be addressed. The use of metal cations produce higher effectiveness as compared to the non-catalytic routes, but water contamination by metals turned out to be a major drawback [17–19]. Significant improvements were registered in the presence of

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Review

Advances in catalytic oxidation of organic pollutants – Prospects for thorough mineralization by natural clay catalysts

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ABSTRACT

This review is devoted to oxidative water treatments, with emphasis on catalytic ozonation. The approach tackled herein resides in exposing a wide variety of oxidative treatments attempts as a basis for summarizing the main findings that allow envisaging improvements aiming towards total mineralization of organic pollutants. Comparison between specific operating conditions for specific pollutant-catalyst-oxidizing systems is quite difficult, and is not targeted in the present work. However, when deeply and judiciously analyzed, such a comparison allows demonstrating that, except for some works, most of these attempts seldom took into accounts basic requirements such as the parameter interactions, the role of cation mobility around a solid surface, if any, the multiple pollutant-catalyst-oxidizing species interactions and the significant contribution of adsorption, etc. Otherwise, how to explain that many experiments are still conducted with unsuitable catalysts under totally inadequate operating conditions? A better understanding of the essential requirements for a catalyst to achieve total mineralization of any organic molecules is the main objective of this work.

The data summarized herein allow devoting a special interest to ozone, which is a powerful oxidizing agent and probably the most easily handleable, in spite of its low solubility in water. The use of catalysts is an ultimate strategy to improve the ozonation performance, by reducing the chemical oxygen demand (COD), even until total disappearance. However, solid catalysts, more particularly those developing high specific surface areas, such as silicates, aluminosilicates, zeolites, pseudozeolites, and clay minerals and derivatives are expected to display appreciable performances in ozonation. The latest findings show strong dependency of their catalytic activity on the chemical and physical characteristics of their surface, their concentration in the liquid media, the pH level of the reaction mixture and other parameters. The effects of these factors will be systematically examined in this review paper. The state-of-the-art in the catalytic ozonation of organic pollutants may be useful to understand the contribution of both surface and bulk ozonation reaction in the vicinity of the surface of a solid catalyst, and more particularly the role of the catalytic agent and its mobility near the solid surface. A rigorous data synthesis, made available in the present paper, allows understanding the ozone scavenging by the very species present in water, and correlating the highest effectiveness of ozone in the presence of optimum catalyst concentration at optimum pH. This supposes strong interactions between the main factors, which remain to be elucidated for each type of catalyst.

The structure of this review makes emphasis on montmorillonite, which exhibits most of the required properties for effective ozonation catalysts. These are common features of natural clay minerals and zeolites, which appear as interesting candidates for large-scale water treatments, targeting complete mineralization of organic pollutants without generating persistent toxins.

Contents

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Total mineralization of sulfamethoxazole and aromatic pollutants through Fe^{2+}-montmorillonite catalyzed ozonation

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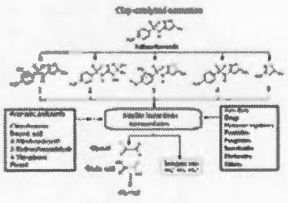
HIGHLIGHTS

- Ozonation in the presence of Fe^{2+} loaded clays can produce toxin-free waters.
- Total mineralization of sulfamethoxazole is possible via catalytic ozonation.
- Aromatic pollutants decompose similarly regardless to their molecular weight.
- The reactivity towards ozone increases with increasing molecular size.
- The reactivity towards ozone increases with decreasing oxidation state.

GRAPHICAL ABSTRACT



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ABSTRACT

The catalytic activity and selectivity of montmorillonite exchanged with Na^+, Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} cations were comparatively investigated in the ozonation of sulfamethoxazole (SMX). Chlorobenzene, benzoic acid, 4-nitrobenzoic acid, 3-hydroxybenzaldehyde, 4-nitrophenol and phenol were used as probe molecules having structural similarity with SMX oxidation intermediates. UV–vis spectrophometry and chemical oxygen demand (COD) measurements showed that Fe(II)–Mt and, to a lesser extent, Co(II)–Mt produce total mineralization of all organic substrates in less than 40 min. Combined HPLC–mass spectrometry revealed a reverse proportionality between the degradation time and molecular size of the organic substrates. Oxalic acid was recognized as a common bottleneck in the ozonation of any organic substrates. Ozonation initially obeyed a first order kinetics, but adsorption took place after 3–5 min, inducing changes in the mechanisms pathways. These findings may be useful for tailoring optimum oxidative treatment of waters without accumulation of hazardous derivatives.

1. Introduction

Human activities are major sources of a wide variety of organic pollutants with hazardous effects on human health and biodiversity [1–7]. At high concentrations, common organic contaminants can be eliminated by conventional techniques such as adsorption, liquid–liquid extraction, coagulation–flocculation and others,

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